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# THE BIREFRINGENCE PATTERNS OF CRYSTAL SPHERES

By Sir C. V. Raman

(*Memoir No.* 82 *of the Raman Research Institute, Bangalore* 6)

Received January 7, 1956)

The preparation of polished spheres of crystalline solids is an ancient art, and indeed it is not uncommon to find large spheres of quartz as exhibits in natural history museums. Using appropriate techniques, it is possible to prepare spheres with different materials and of any desired size, even as small as half a centimetre in diameter. A spherical shape is evidently the most appropriate for a crystal to possess if we wish to observe or exhibit the variation of its optical properties with the direction of propagation of light over the entire possible range. Hence, a collection of such spheres is a useful acquisition for a crystallographic museum.

We may mention here as an example the case of the well-known pleochroic mineral iolite. Holding a polished sphere of this crystal so that it can be turned round and viewed against an extended source of light with a magnifier, Brewster's brushes can be seen around each of the two optic axes in the rear of the sphere. More generally, we place a crystal between a polariser and an analyser, *viz.*, two sheets of polaroid, and view it against an extended source of light. An arrangement should be provided for holding the sphere and altering its setting as desired. The birefringent pattern then seen in various settings shows at once whether the crystal is uniaxial or biaxial, whether the birefringence is weak or strong, whether the material is or is not optically active, and in the case of a biaxial crystal, what the angle between the optic axes is and how their positions vary with the wave-length of the light.

The plates accompanying the present paper illustrate some typical examples of such birefringent patterns. Plates I and II refer to the case of quartz in different settings, Plate III to beryl, Plate IV to calcite, Plate V to topaz, and Plate VI to the case of iolite already mentioned. The spheres used in this study were prepared at this Institute by Mr. J. Padmanabhan who also photographed the birefringence patterns, using for this purpose the monochromatic illumination furnished by a sodium vapour lamp. The principal difficulty encountered in the work was that of obtaining material for preparing the spheres which besides being of adequate size had also the

requisite degree of optical perfection. Any imperfections inevitably show up in the birefringence patterns. This is evident, for example, from the slight irregularities noticeable in the figures recorded for beryl and topaz in Plates III and V respectively.

By way of explanation of the observed effects, we may remark that a beam of light incident on a sphere and traversing it along a diameter would be brought to a focus at a point outside the sphere and at a distance from it depending upon the refractive index. Since there are two refractive indices for any given direction of propagation within a crystal, the positions of the two foci would be different except in the special cases when the direction of propagation within the crystal coincides with an axis of single-wave velocity. Hence, in all directions other than these axes the optical paths would be different for the two indices and interferences can therefore arise. The convergence of the light beams produced by the sphere would result in these interferences appearing in good focus on the surface of a sphere concentric with the crystal sphere but of larger diameter. Hence, when the sphere is rotated, the pattern would rotate with it, and its appearance as seen in any given direction would alter progressively.

With white light, the interferences in the vicinity of the axes of single wave-velocity exhibit colours. They are very fine in the case of calcite (Plate IV) but can be readily seen through a magnifier. These rings can also be seen with a magnifier in the case of topaz but not visible in the photographs of low magnification reproduced in Plate V. As seen through a magnifier, they appear unsymmetrically located with respect to the optic axes, evidently as the result of the dispersion of these axes.

Of a different nature are the circular or elliptic interference rings observed with the various crystals in directions very remote from the axes of single-wave velocity (see Figs. 5 and 6 in Plate I, Figs. 3, 4, 5 and 6 in Plate II, Figs. 5 and 6 in Plate III and Figs. 7 and 8 in Plate V). These interferences are only seen in monochromatic light and hence correspond to large differences of path between the two sets of waves which overlap.

Fig. 4 in Plate II is of special interest. It was recorded when the optic axis of the quartz sphere was set accurately parallel to the vibration direction of the polariser, the analyser also being accurately crossed with respect to it. It will be seen that the rings have not vanished even in this critical setting, but are faintly visible. Their visibility may be ascribed to the non-extinction of the transmitted light consequent on the optical activity of quartz in a direction transverse to the optic axis.

FIG. 1

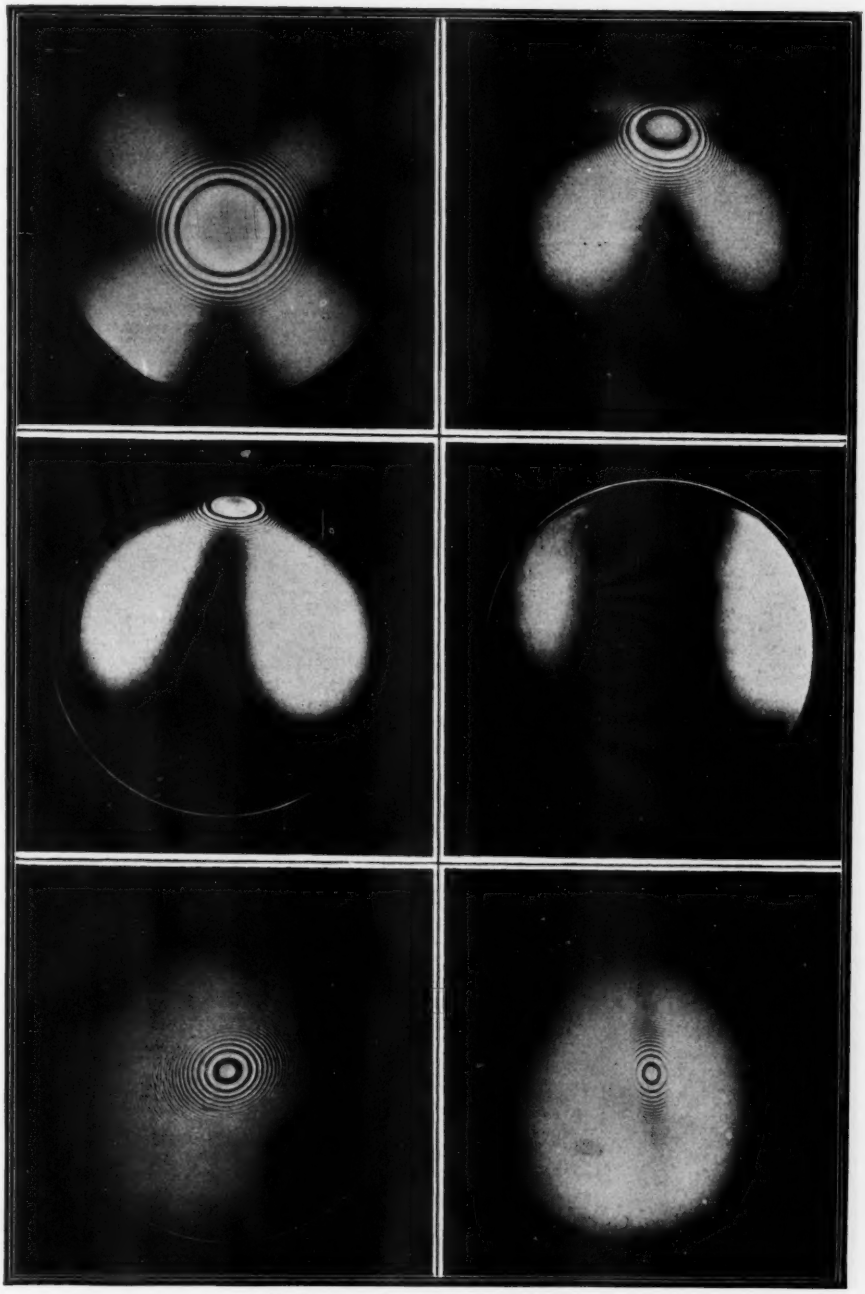


FIG. 2

FIG. 3

FIG. 4

FIG. 5

FIG. 6

Birefringence Patterns of Quartz Sphere

FIG. 1

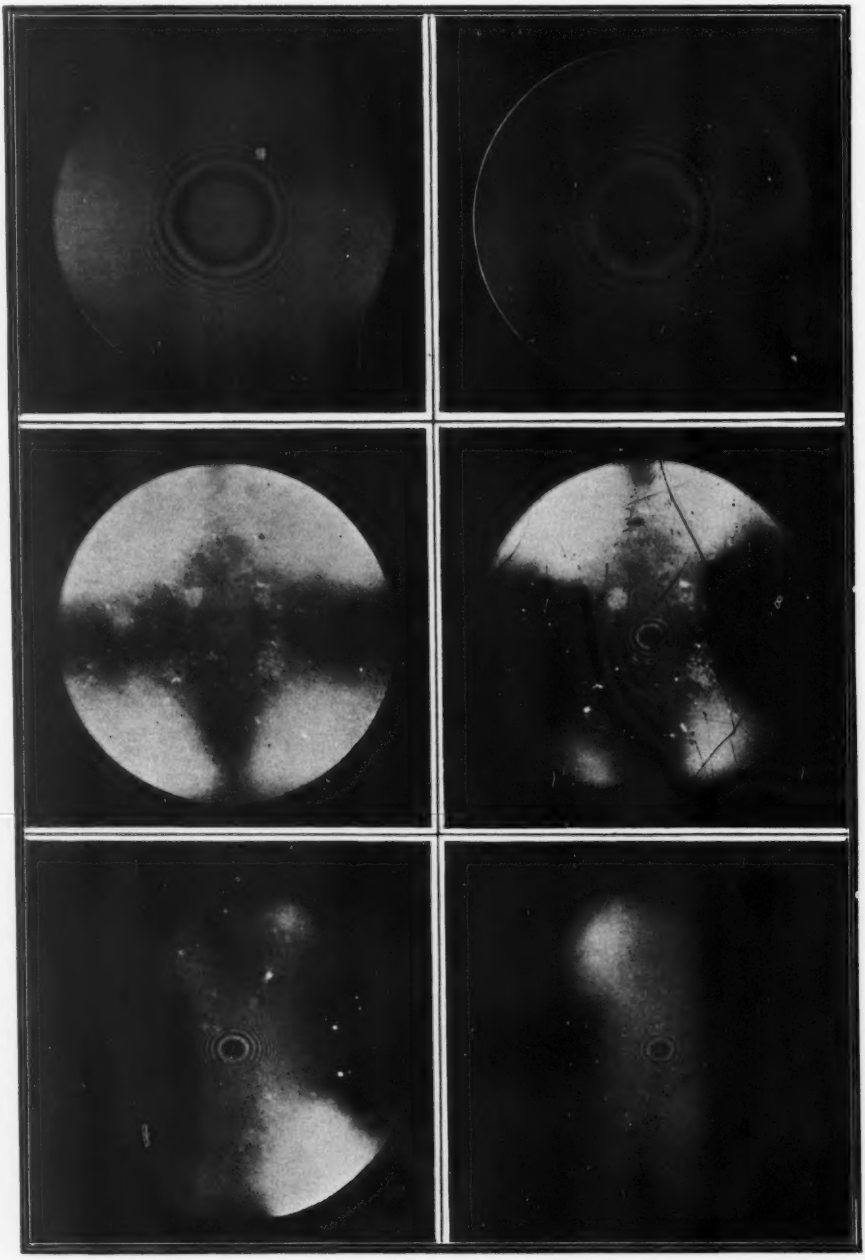


FIG. 2

FIG. 3

FIG. 4

FIG. 5

FIG. 6

Birefringence Patterns of Quartz Sphere

FIG. 1

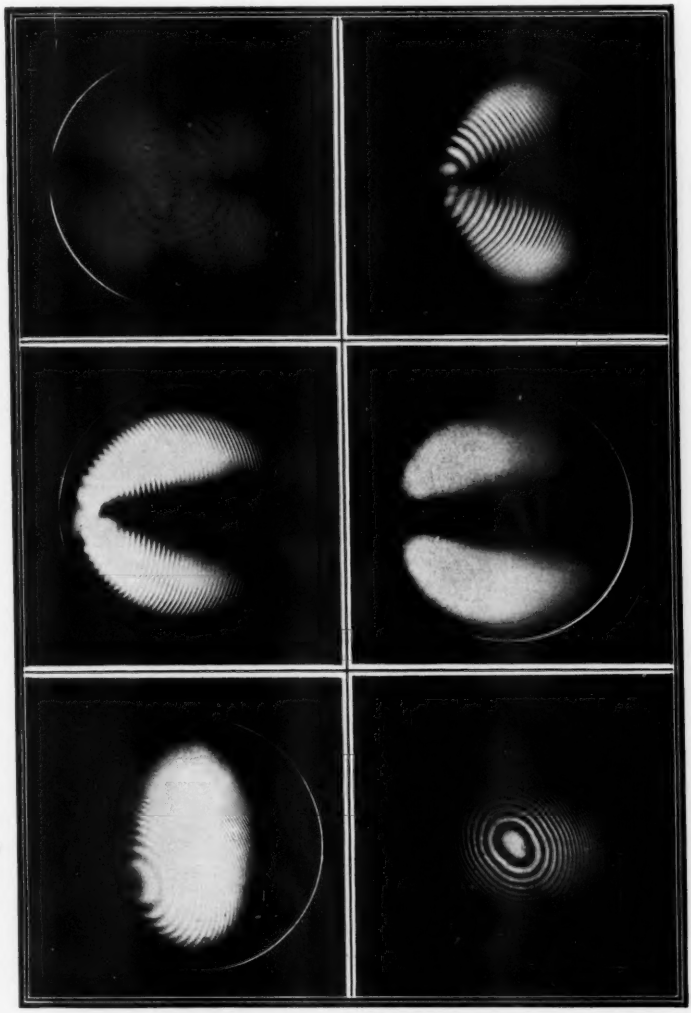


FIG. 2

FIG. 3

FIG. 4

FIG. 5

FIG. 6

Birefringence Patterns of BERYL Sphere

FIG. 1

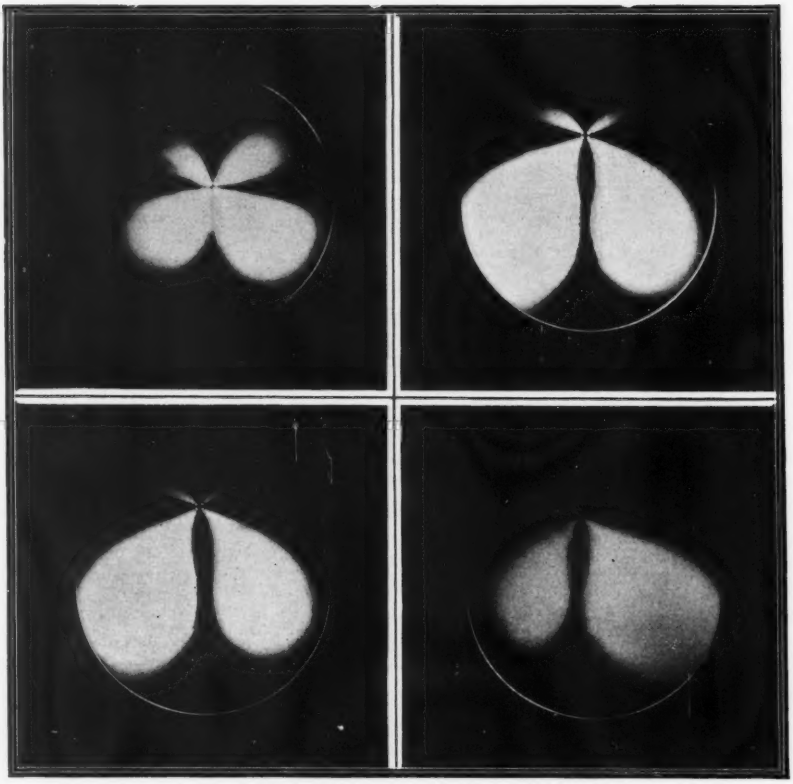


FIG. 2

FIG. 3

FIG. 4

Birefringence Patterns of Calcite Sphere

FIG. 1

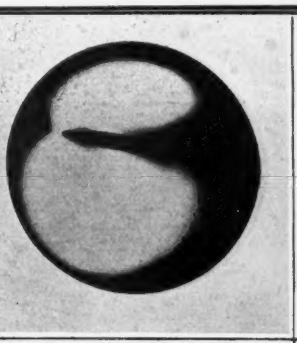


FIG. 2

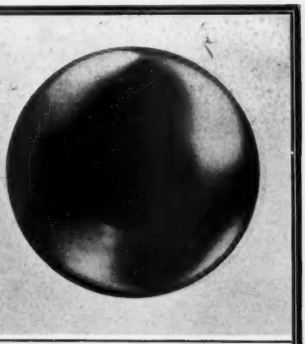


FIG. 3

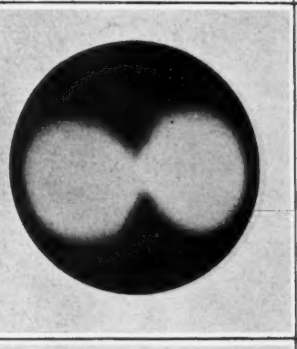


FIG. 4

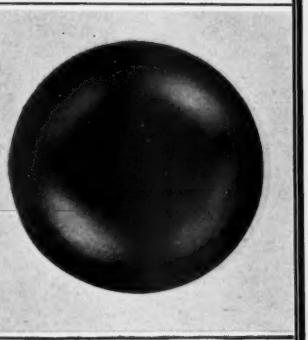


FIG. 5

FIG. 6

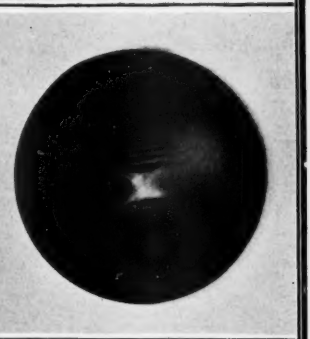
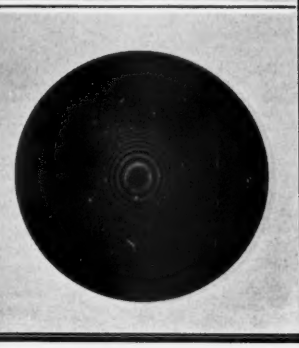


FIG. 7

FIG. 8



Birefringence Patterns of Topaz Sphere

FIG. 1

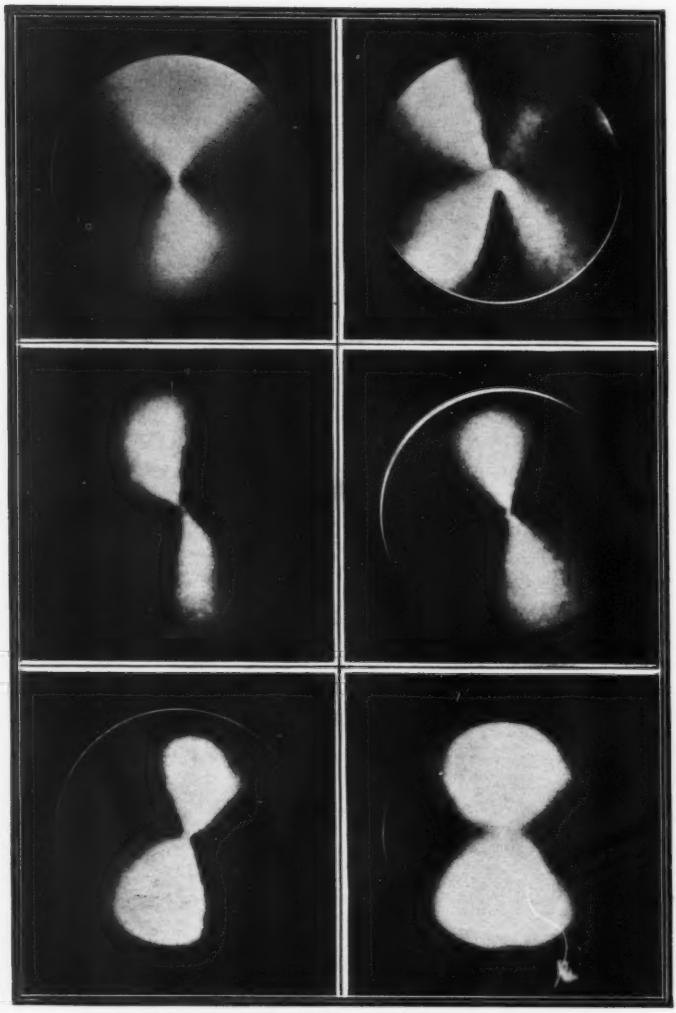


FIG. 2

FIG. 3

FIG. 4

FIG. 5

FIG. 6

Birefringence Patterns of IOLITE Sphere

Fig. 1 in Plate VI represents Brewster's brushes as exhibited by iolite without any polariser or analyser. Similar brushes running parallel to them are also seen in the vicinity of the other axis of single-wave velocity. The other figures in Plate VI exhibit the effects of introducing either a polariser or an analyser, or both between the source of light and the eye of the observer.

SUMMARY

Light from an extended source traversing a sphere reaches foci lying on a concentric spherical surface of a larger radius determined by the refractive index. Hence, if the incident light be polarised and the sphere is viewed through an analyser, the interferences arising from the birefringence of the material are focussed by the sphere itself on such concentric surface and rotate with the sphere when the latter is rotated. Photographs of such patterns in typical cases are reproduced.

# ORDINARY LINEAR DIFFERENTIAL EQUATIONS INVOLVING RANDOM FUNCTIONS

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Received December 5, 1955
(Communicated by Dr. Alladi Ramakrishnan)

## Abstract

Physical processes which can be represented by symbolic differential equations involving random functions are cited and studied. The solutions of these equations are obtained using Ramakrishnan's recent phenomenological interpretation of integrals of random functions.

In this paper, we study various physical processes that can be represented by ordinary differential equations involving random functions of the parameter with respect to which the differential coefficients are defined. Such a study has been made possible in view of Ramakrishnan's recent phenomenological interpretation of integrals of random functions (Ramakrishnan, 1955).

The present method, based on that interpretation, is applicable to processes represented by stochastic variables which satisfy differential equations involving random functions, provided the solution of the equations can be put in the form of simple or iterated integrals of these random functions. Such iterated integrals have already been discussed earlier by Ramakrishnan (1955) and the authors (1955) without any special reference to differential equations. In spite of the risk of possible repetition in some cases, it is considered worthwhile to deal with these processes defined by solutions of linear differential equations.

## General Method of Solution

Let us consider the linear differential equation of $m$-th order,

$$\frac{d^m Y}{dt^m} + \lambda_1(t)\frac{d^{m-1}Y}{dt^{m-1}} + \ldots + \lambda_m(t)\,Y = \kappa(t)\,X(t), \qquad (1)$$

where $\lambda_i(t)$'s and $\kappa(t)$ are fully determinate functions of $t$, and $X(t)$ is a random function of $t$. The problem of studying the distribution of Y given the distribution of X is indeed a very difficult one. However, the problem

can be treated quite satisfactorily, if we are able to obtain the solution of (1) in the form

$$Y = \phi_m(t) \int_0^t \phi_{m-1}(t_{m-1})\, dt_{m-1} \int_0^{t_{m-1}} \phi_{m-2}(t_{m-2})\, dt_{m-2} \ldots \int_0^{t_1} \phi_0(t_0)\, \kappa(t_0)\, X(t_0)\, dt_0. \tag{2}$$

The passage from (1) to (2) for any general $m$ is by itself a difficult problem except in the special case when all the $\lambda$'s are constants and in this paper an attempt is made for the case $m = 2$ (see Appendix A). It is interesting to note that the solutions of a number of equations of type (1) representing physical processes are capable of being expressed in the form (2).

Y as given by (2) is an $m$-th iterated integral of a random function, and the normal interpretation of such integrals given recently by Ramakrishnan is based on the concept of the " trajectory " or curve of growth of a stochastic process. In any typical realisation of the process $X(\tau)$, we ' plot ' the value of the random function $X(\tau)$ in the interval $(o, t)$ and thus obtain the realised trajectory. By a simple extension of the theory of Riemann integration, the realised value of the symbolic integral $\int_0^t X(\tau)\, d\tau$ corresponding to the given realisation of $X(\tau)$ is now defined as the area enclosed by the curve $X(\tau)$, the $\tau$-axis and the ordinates at $\tau = 0$ and $\tau = t$. Iterated integrals of $X(\tau)$ can be defined similarly. If we wish to obtain the probability frequency function of $\int_0^t X(\tau)\, d\tau$ [or of iterated integrals of $X(\tau)$] we have to assign a probability measure to the trajectory of $X(\tau)$ in the interval $(o, t)$ and this is known to be a very difficult mathematical problem. However, if we confine ourselves to a simple random function $X(\tau)$ which represents a " basic random process "—a Markoff process, homogeneous with respect to $\tau$, whose typical trajectory is characterised by a finite number of discrete transitions, the trajectory remaining parallel to the $\tau$ axis between two transitions—it is possible to assign a measure to its trajectory. Many physical processes whose trajectories are continuous can therefore be studied by considering the stochastic variables involved as iterated integrals of a basic random process or by approximating the variables to such integrals. Even if $X(t)$ is not a basic random process, we can readily obtain the moments and correlation functions of iterated integrals of $X(t)$ by the use of a theorem due to Ramakrishnan (1954 *a*).

The random variable Y as defined in (2) has been dealt with by the authors (1955) for the special case, $X(\tau) = dn(\tau)/d\tau$ where $n(\tau)$ represents a Poisson process, *i.e.*, $n(\tau)$ has value $n$ with probability $e^{-\lambda\tau}(\lambda\tau)^n/n!$

where $\lambda$ is the parameter of the process. $dn(\tau)/d\tau$ in such a case has a specialised meaning which will be explained presently. The Laplace transform solution of the p.f.f. of Y has been explicitly obtained in that paper and here we shall make use of the solution to obtain the moments in particular cases of physical interest.

### LINEAR DIFFERENTIAL EQUATION OF THE FIRST ORDER

Let us consider a stochastic variable $Y(t)$ ($t$ is the parameter with respect to which the physical process we have to deal with progresses) defined by

$$\frac{dy}{dt} + \lambda_1(t)\, Y = \kappa(t)\, X(t), \tag{3}$$

where $\lambda_1(t)$ and $\kappa(t)$ are fully determinate functions of $t$, and $\kappa(t)$ is a random variable representing a process progressing with $t$. Our object is to obtain the p.f.f. of $Y(t)$, or its moments—at least the first few—given the nature of the process $X(t)$. The first step consists in formally writing the solution of (3) as

$$Y(t) - Y_0 e^{-\mu(t)} = Y'(t) = \int_0^t e^{-\{\mu(t)-\mu(\tau)\}}\, \kappa(\tau)\, X(\tau)\, d\tau, \tag{4}$$

as if $X(t)$ were a determinate function. $\mu(t)$ is given by

$$\mu(t) = \int_0^t \lambda_1(\tau)\, d\tau \tag{5}$$

The initial condition is defined as $Y(t) \equiv Y_0$ at $t = 0$.

We shall now consider particular cases of $X(t)$.

(i) $X(t) = \dfrac{dn(t)}{dt}$ *where* $n(t)$ *represents a Poisson Process.*

It is well known that corresponding to a realisation of events at $t_1, t_2, \ldots, t_n$ along the $t$-axis, the realised value of $dn(t)/dt$ is given by

$$\sum_i \delta(t - t_i)$$

where $\delta$ is the Dirac-delta function. The distribution of $Y'(t) = Y - Y_0 e^{-\mu(t)}$ has been studied by the authors (1955).

Defining the Laplace transform $p(s; t)$ of $\pi(Y'; t)$, the probability frequency function of $Y'(t)$, as

$$p(s; t) = \int_0^\infty e^{-sY'}\, \pi(Y'; t)\, dY', \tag{6}$$

the solution for $p(s;t)$ was obtained there as

$$p(s;t) = \exp\ [-\lambda t + \lambda \int_0^t \exp\{-s\kappa(\tau)\, e^{-[\mu(t)-\mu(\tau)]}\}\, d\tau]. \tag{7}$$

Moments of $Y - Y_0 e^{\mu(t)}$ and hence those of Y can be obtained from (7).

An example of such a process is provided by the fluctuation of voltage at the anode of a thermionic valve due to the fluctuations in the number of electrons per unit time emitted by the cathode (Moyal, 1950). If we assume the probability of emission of an electron per unit time to be constant, we may reasonably expect the number $n(t)$ of electrons emitted in the interval $(0, t)$ to be governed by the Poisson distribution. The fluctuating voltage $V(t)$ across C satisfies the equation

$$\frac{dV}{dt} + \frac{V}{RC} = -\frac{\epsilon}{C}\frac{dn}{dt} \tag{8}$$

where we have assumed that the circuit between anode and earth is equivalent to a resistance R in parallel with a capacity C. $\epsilon$ is the charge of the electron. Substituting the values of $\lambda(t)$, $\kappa(t)$ (which are constants in this particular case) in (7) the Laplace transform solution of $\pi(V;t)$ the p.f.f. of V is obtained as

$$p(s;t) = \exp\left[-n_0 t + n_0 \int_0^t \exp\left\{\frac{s\epsilon}{C}\, e^{-(t-\tau)/RC}\right\} d\tau\right], \tag{9}$$

where $n_0$ is the mean number of electrons emitted per unit time.

The moments are given by

$$E\{V(t) - V_0 e^{-t/RC}\} = -n_0 \epsilon R\,(1 - e^{-t/RC}),* \tag{10}$$

$$E\{[V(t) - V_0 e^{-t/RC}]^2\} = n_0^2 \epsilon^2 R^2 (1 - e^{-t/RC})^2 + \frac{n_0 \epsilon^2 R}{2C}\,(1 - e^{-2t/RC}), \tag{11}$$

$$E\{[V(t) - V_0 e^{-t/RC}]^m\} =$$

$$n_0 \sum_{r=0}^{m-1} \left(-\frac{\epsilon}{C}\right)^{m-r} E\{[V(t) - V_0 e^{-t/RC}]^r\} \frac{(1-e^{t(m-r)/RC})RC(m-1)!}{(m-r-1)!\,r!} \tag{12}$$

(ii) $X(t)$ represents a 'Q' process.

---

* Throughout this paper E denotes expectation value.

A 'Q' process is defined as follows: Consider the distribution of random points on a line representing the $t$-axis, according to a Poisson distribution with parameter $\lambda$. Let the value $q_i$ be associated with the $i$-th point, all the $q_i$'s having the same probability frequency function $\phi(q)$. Then the Q-process is defined by the stochastic variable

$$Q(t) = q_1 q_2 \ldots . q_n \tag{13}$$

which is associated with the interval $(0, t)$ when $n$ points are realised in $(0, t)$.

By the application of the theorem established by Ramakrishnan (1954 *a*), the $n$-th moment of $Y - Y_0 e^{-\mu(t)}$ as defined in (4) when $X(t) \equiv Q(t)$ is given by

$$\begin{aligned} E\{(Y - Y_0 e^{-\mu(t)})^n\} = \int_0^t \int_0^t \ldots . \int_0^t E\{Q(\tau_1) Q(\tau_2) \ldots . Q(\tau_n)\} \\ \kappa(\tau_1) \kappa(\tau_2) \ldots . \kappa(\tau_n) \exp[-n\mu(t) + \mu(\tau_1) + \mu(\tau_1) + \ldots . + \\ + \mu(\tau_n)] \, d\tau_1 \, d\tau_2 \ldots . d\tau_n, \end{aligned} \tag{14}$$

where

$$\begin{aligned} E\{Q(\tau_1) Q(\tau_2) \ldots . Q(\tau_n)\} = \exp[-\lambda\{(1 - q_n)\tau_1 + (1 - q_{n-1}) \\ (\tau_2 - \tau_1) + \ldots . + (1 - q_1)(\tau_n - \tau_{n-1})\}], \\ (0 < \tau_1 < \tau_2 < \ldots . < \tau_n), \end{aligned} \tag{15}*$$

$$q_n = E\{q^n\} = \int_q q^n \phi(q) \, dq. \tag{16}$$

Such a Q process occurs for example in statistical astronomy. If we assume that interstellar matter consists of discrete clouds, $q$ being the transparency factor of a single cloud, then Q is the cumulative transparency factor of an aggregate of clouds occurring in a Poisson manner. If it is further assumed that the amount of light radiation from an element of length $d\tau$ at $\tau$ along the line of sight of an observer at $t = 0$ is $d\tau$ (*i.e.*, a uniform distribution of sources exists), then $Y(t)$, the total intensity reaching the observer from the system extending from 0 to $t$ satisfies equation (3), with $\lambda_1(t) = 0$, $\kappa(t) = 1$ and $Y(0) \equiv 0$. The moments of Y have been obtained by Ramakrishnan (1954 *b*). The correlation function of Y of degree $n$ is given by

$$\begin{aligned} E\{Y(t_1) Y(t_2) \ldots . Y(t_n)\} \\ = \int_0^{t_1} \int_0^{t_2} \ldots . \int_0^{t_n} E\{Q(\tau_1) Q(\tau_2) \ldots . Q(\tau_n)\} \, d\tau_1 \, d\tau_2 \ldots . d\tau_n. \end{aligned} \tag{17}$$

* For a derivation of this result, see Alladi Ramakrishnan (1954 *b*).

We note that the explicit expression (15) for the correlation function can be written down only after the variables are ordered. In the integration of the expression (17), we have to take into consideration the relative order of the $n$ variables $\tau_1, \tau_2, \ldots, \tau_n$. Hence in the process of integration, the range of integration of each of the variables is split up into intervals $(0, t_1)$, $(t_1, t_2), \ldots, (t_{n-1}, t_n)$; $(t_1 < t_2 < \ldots < t_n)$, and the resulting $n$-fold integrals computed in the ranges one by one. Use is also made of the following well-known lemma on ordering of the variables of integration.

$$\int_0^t \int_0^t \ldots \int_0^t f(X_1, X_2, \ldots, X_n)\, dX_1\, dX_2 \ldots dX_n$$

$$= n! \int_0^t dX_1 \int_{X_1}^t dX_2 \ldots \int_{X_{n-1}}^t f(X_1, X_2, \ldots, X_n)\, dX_n, \tag{18}$$

where $f$ is symmetrical in all the variables $X_1, X_2, \ldots, X_n$. The correlation functions of degree two and three have been evaluated by this method. These are given in a paper by Alladi Ramakrishnan and S. K. Srinivasan (1956) for the particular case when $\phi(q') = \delta(q' - q)$, but the same expressions are valid for any general $\phi(q)$ if $q^r$ is replaced by $q_r$ everywhere in them.

(iii) *$X(t)$ represents a fluctuating density field : (F.D.F.).*

Recently, the concept of a wildly fluctuating field has been introduced by Chandrasekhar and Munch (1952) and studied in great detail by Ramakrishnan (1954). Here we recall some of the results obtained by Ramakrishnan. Let $\pi(X' \mid X; \mid t' - t \mid)dX'$ be the conditional probability that the density $X(t)$ (considered as a stochastic variable) has a value $X'$ at $t'$ given that it had a value $X$ at $t$; we assume that $\pi(X' \mid X; \mid t' - t \mid) \to R(X' \mid X) \cdot \mid t' - t \mid$ as $\mid t' - t \mid \to 0$ and also that $R(X' \mid X)$ is a function of $X'$ alone, and write $R(X' \mid X) = R(X')$. Ramakrishnan has proved that

$$\pi(X' \mid X; \mid t' - t \mid) = \frac{R(X')}{a}(1 - e^{-a\mid t' - t \mid}) + \delta(X' - X)\, e^{-a\mid t' - t \mid}, \tag{19}$$

where

$$a = \int_{X'} R(X')\, dX' \tag{20}$$

Note as $\mid t' - t \mid \to \infty$, $\pi(X' \mid X; \mid t' - t \mid) \to \frac{R(X')}{a} = \psi(X')$. (21)

The concept of wild fluctuation is introduced by making $a$ very large. In this case $\pi \to \psi$ for $\mid t' - t \mid >> 1/a$ and hence the distribution at $t'$ is effectively independent of the distribution at $t$. But it is to be noted that however

large $a$ may be, the densities are not independent in the range $0<|t'-t|<1/a$. Hence in any process of integration over the $t$-space (this has to be carried out if we desire to obtain the moments of integrals associated with X) a correlation exists and contributes a correction term of the order of $1/a$ when $a$ is very large. The correction term is taken care of by replacing $e^{-a(t'-t)}$ by $1/a\ \delta(t'-t)$ in (19).

We now consider physical processes represented by (3) when $X(t)$ represents an F.D.F. For a free particle (of mass $m$, velocity $v$) the equation of motion is

$$m\frac{dv}{dt}+fv=F(t), \tag{22}$$

where $f$ is the frictional force and $F(t)$ is an F.D.F. defining the random force (Wang and Uhlenbeck, 1945). Again, the current $i$ in an R — L circuit satisfies a similar equation. If a body of thermal capacity C is connected to its surroundings by a thermal resistance R, the temperature difference $\theta$ between the body and the surroundings (which are supposed to form a " heat-bath ") satisfies the equation (MacDonald, 1948–49)

$$C\frac{d\theta}{dt}+\frac{1}{R}\ \theta=H(t), \tag{23}$$

where $H(t)$ is an F.D.F. defining the flow of heat.

Investigations of these processes by the workers mentioned above and by others are confined only to the first two moments in the stationary case (*i.e.*, $t\to\infty$).

All these processes will now be studied by taking $\lambda_1(t)$ and $\kappa(t)$ as constants in (3). Then (4) takes the form

$$Y-Y_0e^{-\lambda_1 t}=\kappa\int_0^t e^{-\lambda_1(t-\tau)}X(\tau)\,d\tau. \tag{24}$$

As we are interested in the stationary case, *i.e.*, $t\to\infty$, the second term on the LHS can be neglected. The $n$-th moment of Y is given by

$$E\{Y^n\}=\lim_{t\to\infty}\kappa^n\int_0^t\int_0^t\ldots\int_0^t e^{-\lambda_1(nt-\tau_1-\tau_2-\ldots-\tau_n)}$$

$$E\{X(\tau_1)X(\tau_2)\ldots X(\tau_n)\}\,d\tau_1\,d\tau_2\ldots d\tau_n \tag{25}$$

By definition,

$$\mathrm{E}\{\mathrm{X}(\tau_1)\,\mathrm{X}(\tau_2)\ldots.\mathrm{X}(\tau_n)\} = \int_{\mathrm{X}_n}\int_{\mathrm{X}_{n-1}}\ldots.\int_{\mathrm{X}_1}\mathrm{X}_1\,\mathrm{X}_2\ldots.\,\mathrm{X}_n$$

$$\pi\,(\mathrm{X}_n, \mathrm{X}_{n-1}, \ldots., \mathrm{X}_1 \mid \mathrm{X}_0\,;\, \tau_n, \tau_{n-1}, \ldots., \tau_1)\,d\mathrm{X}_1\,d\mathrm{X}_2\ldots.d\mathrm{X}_n$$

$$= \int_{\mathrm{X}_n}\int_{\mathrm{X}_{n-1}}\ldots.\int_{\mathrm{X}_1}\mathrm{X}_1\,\mathrm{X}_2\ldots.\mathrm{X}_n\,\pi\,(\mathrm{X}_n \mid \mathrm{X}_{n-1};\, \tau_n - \tau_{n-1})$$

$$\pi\,(\mathrm{X}_{n-1} \mid \mathrm{X}_{n-2};\, \tau_{n-1} - \tau_{n-2})\ldots.$$

$$\ldots.\pi\,(\mathrm{X}_1 \mid \mathrm{X}_0;\, \tau_1)\,d\mathrm{X}_1\,d\mathrm{X}_2\ldots.\,d\mathrm{X}_n. \qquad (26)^*$$

Now, the exponential factor in the integral in (25) vanishes as $t \to \infty$ except for values of $\tau_1, \tau_2, \ldots., \tau_n$ which keep $(nt - \tau_1 - \tau_2 - \ldots. - \tau_n)$ finite; hence the whole contribution to the integral comes from the region where values of $\tau_1, \tau_2, \ldots., \tau_n$ all tend to infinity. The differences $\tau_i - \tau_{i-1}$ $(i = 1, 2, 3, \ldots., n)$ are all however considered finite. Consequently in the expression (26) for $\mathrm{E}\{\mathrm{X}(\tau_1)\,\mathrm{X}(\tau_2)\ldots.\mathrm{X}(\tau_n)\}$ which is to be fed into (25), we put

$$\pi\,(\mathrm{X}_1 \mid \mathrm{X}_0;\, \tau_1) = \psi\,(\mathrm{X}_1), \qquad (27)$$

since only values of $\tau_1$ tending to infinity are significant for our purpose, as explained above, while for the remaining factors $\pi\,(x_i \mid x_{i-1};\, \tau_i - \tau_{i-1})$ we have to substitute from (19) because $\tau_i - \tau_{i-1}$ is finite.

We then have,

$$\mathrm{E}\{\mathrm{X}(\tau_1)\,\mathrm{X}(\tau_2)\ldots.\,\mathrm{X}(\tau_n)\} = \int_{\mathrm{X}_1}\int_{\mathrm{X}_2}\ldots.\int_{\mathrm{X}_n}\mathrm{X}_1\mathrm{X}_2\ldots.\mathrm{X}_n\left[\psi\,(\mathrm{X}_1)\,\psi\,(\mathrm{X}_2)\ldots.\right.$$

$$\left.\ldots.\psi\,(\mathrm{X}_n)\left\{1 - \frac{1}{a}\sum_i \delta\,(\tau_i - \tau_{i-1})\right\} + \frac{1}{a}\sum_i \frac{\psi\,(\mathrm{X}_1)\,\psi\,(\mathrm{X}_2)\ldots\psi\,(\mathrm{X}_n)}{\psi\,(\mathrm{X}_i)}\right.$$

$$\left.\delta\,(\mathrm{X}_i - \mathrm{X}_{i-1})\,\delta\,(\tau_i - \tau_{i-1}) + \mathrm{O}\left(\frac{1}{a^2}\right)\right]d\mathrm{X}_1\,d\mathrm{X}_2\ldots.\,d\mathrm{X}_n. \qquad (28)$$

Introducing the expression (28) into the right hand side of (25), we obtain after some calculation

$$\mathrm{E}\{\mathrm{Y}^n\} = \left[\mathrm{E}\{\mathrm{Y}\}\right]^n + \left[\mathrm{E}\{\mathrm{Y}\}\right]^{n-2}\frac{n\,(n-1)\kappa}{2a\lambda_1}\left[\mathrm{E}\{\mathrm{X}^2\} - (\mathrm{E}\{\mathrm{X}\})^2\right] \qquad (29)$$

where

$$\mathrm{E}\{\mathrm{X}^n\} = \int_{\mathrm{X}}\mathrm{X}^n\,\psi\,(\mathrm{X})\,d\mathrm{X}. \qquad (30)$$

* In this paper the symbol $f_{\mathrm{X}}$ means integration over the whole range of the variable X.

In particular when $n = 2$,

$$\mathrm{E}\{\mathrm{Y}^2\} = \left[\mathrm{E}\{\mathrm{Y}\}\right]^2 + \frac{\kappa}{a\lambda_1}\left[\mathrm{E}\{\mathrm{X}^2\} - (\mathrm{E}\{\mathrm{X}\})^2\right]. \tag{31}$$

(29) can be written as

$$\mathrm{E}\{\mathrm{Y}^n\} = \left[\mathrm{E}\{\mathrm{X}\}\right]^n + \frac{n(n-1)}{2}\left[\mathrm{E}\{\mathrm{Y}^2\} - (\mathrm{E}\{\mathrm{Y}\})^2\right](\mathrm{E}\{\mathrm{Y}\})^{n-2}. \tag{32}$$

## LINEAR DIFFERENTIAL EQUATION OF THE SECOND ORDER

We proceed to discuss the case where $\mathrm{Y}(t)$ satisfies the second order linear differential equation

$$\frac{d^2\mathrm{Y}}{dt^2} + \lambda_1(t)\frac{d\mathrm{Y}}{dt} + \lambda_2(t)\,\mathrm{Y} = \kappa(t)\,\mathrm{X}(t), \tag{33}$$

where $\lambda_1(t)$, $\lambda_2(t)$ and $\kappa(t)$ are fully determinate functions of $t$ and $\mathrm{X}(t)$ is a random function as before. The solution of (33) can always be put in the form (see Appendix A)

$$\mathrm{Y} = e^{-\frac{1}{2}\mu(t)}\int_0^t e^{-\{a_2(t)-a_2(\tau)\}}\,d\tau\int_0^\tau e^{+\{a_2(\tau)-a_2(\tau')\}}\,\kappa(\tau')\,\mathrm{X}(\tau')\,d\tau' \tag{34}$$

under proper initial conditions.

We will now consider some particular cases of the function $\mathrm{X}(t)$.

(i) $X(t) = \dfrac{dn(t)}{dt}$ *where* $n(t)$ *is a random variable representing a Poisson Process.*

This has been dealt with by the authors earlier (1955); the Laplace transform of $\pi(\mathrm{Y}; t)$ is given by

$$p(s; t) = \exp\left[-\lambda t + \lambda\int_0^t \exp\{-sf(t, \tau)\,\kappa(\tau)\}\,d\tau\right] \tag{35}$$

where

$$f(t, \tau) = \exp\left[-\tfrac{1}{2}\mu(t) - a_2(t) - a_2(\tau)\right]\int_\tau^t \exp\left[2a_2(\tau')\right]d\tau'. \tag{36}$$

The moments of Y of any order can be readily obtained from (35).

(ii) $\mathrm{X}(t)$ *represents a* '$Q$' *process,* i.e., $X(t) = Q(t)$.

It is convenient to express Y as a single iterated integral. This can be achieved by changing the order of integration of $\tau$ and $\tau'$ on the R.H.S. of (34) and performing the integration over $\tau$. Thus we obtain

$$\mathrm{Y} = \int_0^t \kappa(\tau) f(t, \tau) \mathrm{X}(\tau)\, d\tau, \tag{37}$$

where $f(t, \tau)$ is defined in (36).

The $n$-th moment of Y is given by an expression similar to (14).

A special case of interest is when $\lambda_1(t) \equiv \lambda_2(t) \equiv 0$ and $\kappa(t) = 1$, *i.e.*, $f(t, \tau) = t - \tau$. The first few moments of Y are then given by

$$\mathrm{E}\{\mathrm{Y}(t)\} = \frac{t}{\lambda(1-q_1)} - \frac{1 - e^{-\lambda(1-q_1)t}}{\lambda^2(1-q_1)^2}, \tag{38}$$

$$\begin{aligned}\mathrm{E}\{\mathrm{Y}^2(t)\} = 2\Bigg[&\frac{1}{\lambda(1-q_1)}\left\{\frac{t^2}{\lambda(1-q_2)} - \frac{2t}{\lambda^2(1-q_2)^2} + 2\cdot\frac{1-e^{-\lambda(1-q_2)t}}{\lambda^3(1-q_2)^3}\right\}\\ &- \frac{1}{\lambda^2(1-q_1)^2}\left\{\frac{t}{\lambda(1-q_2)} - \frac{1-e^{-\lambda(1-q_2)t}}{\lambda^2(1-q_2)^2}\right\}\\ &+ \frac{1}{\lambda^2(1-q_1)^2}\left\{\frac{t\,e^{-\lambda(1-q_1)t}}{\lambda(q_1-q_2)} - \frac{e^{-\lambda(1-q_1)t}}{\lambda^2(q_1-q_2)^2} + \frac{e^{-\lambda(1-q_2)t}}{\lambda^2(q_1-q_2)^2}\right\}\Bigg],\end{aligned} \tag{39}$$

$$\begin{aligned}\mathrm{E}\{\mathrm{Y}^3(t)\} = 6\Bigg[&\frac{1}{\lambda^2(1-q_1)(1-q_2)}\left\{\frac{t^3}{\lambda(1-q_2)} - \frac{3t^2}{\lambda^2(1-q_2)^2} + \frac{6t}{\lambda^3(1-q_2)^3}\right.\\ &\left. - 6\cdot\frac{1-e^{-\lambda(1-q_2)t}}{\lambda^4(1-q_2)^4}\right\} - \left\{\frac{1}{\lambda^3(1-q_1)^2(1-q_2)} + \frac{2}{\lambda^3(1-q_1)(1-q_2)^2}\right\}\\ &\left\{\frac{t^2}{\lambda(1-q_2)} - \frac{2t}{\lambda^2(1-q_2)^2} + 2\cdot\frac{1-e^{-\lambda(1-q_2)t}}{\lambda(1-q_2)^3}\right\} + \frac{1}{\lambda^3(1-q_1)^2(q_1-q_2)}\\ &\left\{\frac{t^2\,e^{-\lambda(1-q_1)t}}{\lambda(q_1-q_2)} - \frac{2t\,e^{-\lambda(1-q_1)t}}{\lambda^2(q_1-q_2)^2} + 2\frac{e^{-\lambda(1-q_2)t}}{\lambda^3(q_1-q_2)^3} - 2\frac{e^{-\lambda(1-q_2)t}}{\lambda^3(q_1-q_2)^3}\right\}\\ &+ \left\{\frac{2}{\lambda^4(1-q_1)(1-q_2)^3} + \frac{1}{\lambda^4(1-q_1)^2(1-q_2)^2}\right\}\left\{\frac{t}{\lambda(1-q_2)}\right.\\ &\qquad\left. - \frac{1-e^{-\lambda(1-q_2)t}}{\lambda^2(1-q_2)^2}\right\}\\ &- \left\{\frac{2}{\lambda^4(1-q_1)(1-q_2)^3} + \frac{1}{\lambda^4(1-q_1)^2(1-q_2)^2} - \frac{1}{\lambda^4(1-q_1)^2(q_1-q_2)^2}\right\}\\ &\left\{\frac{t\,e^{-\lambda(1-q_2)t}}{\lambda(q_2-q_2)} - \frac{e^{-\lambda(1-q_2)t} - e^{-\lambda(1-q_2)t}}{\lambda^2(q_2-q_2)^2}\right\} - \frac{1}{\lambda^4(1-q_1)^2(q_1-q_2)^2}\\ &\left\{\frac{t\,e^{-\lambda(1-q_1)t}}{\lambda(q_1-q_2)} - \frac{e^{-\lambda(1-q_1)t} - e^{-\lambda(1-q_2)t}}{\lambda^2(q_1-q_2)^2}\right\}\Bigg].\end{aligned} \tag{40}$$

Ramakrishnan (1955) has proved that in this case $\pi(Y;t)$, the p.f.f. of Y satisfies the equation

$$\frac{\partial \pi(Y;t)}{\partial t} = -\lambda\pi(Y;t) + \lambda \int \pi\left(\frac{Y}{q};t\right) \frac{\phi(q)\,dq}{q} - t\,\frac{\partial \pi(Y;t)}{\partial Y}. \quad (41)$$

If $\rho(s;t)$ be the Mellin's transform of $\pi(Y;t)$ with respect to Y then $\rho(s;t)$ satisfies the equation

$$\frac{\partial \rho(s;t)}{\partial t} = -\lambda\rho(s;t) + \lambda\,\rho(s;t)\,q^{s-1} + t(s-1)\,\rho(s-1;t). \quad (42)$$

The $n$-th moment of Y is given by $\rho(n+1;t)$. The first three moments of Y have also been calculated from (42) and are found to be identical with (38), (39) and (40) as expected.

(iii) $X(t)$ *represents an F.D.F.*

We can use (28) and the $n$-th moment of Y is given by an expression similar to (25). Physical processes represented by (33) when $X(t)$ is an F.D.F. can easily be cited. The distance $s$ traversed by a Brownian particle (of mass $m$) is determined by the equation (Wang and Uhlenbeck, 1945)

$$m\,\frac{d^2s}{dt^2} + f\,\frac{ds}{dt} = F(t), \quad (43)$$

or, considering an example from electricity, the total charge K in an R-L circuit satisfies the equation (McCombie, 1953)

$$L\,\frac{d^2K}{dt^2} + R\,\frac{dK}{dt} = E(t). \quad (44)$$

Again let us consider the fluctuation of $\theta$, the torsion of a suspended coil galvanometer. The equations governing the process are [Jones and McCombie (1952)]

$$I\,\frac{d^2\theta}{dt^2} + k\,\frac{d\theta}{dt} + c\theta = F(t) + Gi, \quad (45)$$

$$L\,\frac{di}{dt} + Ri = E(t) - G\,\frac{d\theta}{dt}, \quad (46)$$

where I is the moment of inertia of the suspended system, $k$ and $c$ are the damping and torsional constants and G is the flux linkage of the coil. $F(t)$ and $E(t)$ in (45) and (46) are F.D.F.'s defining the random couple and random voltage respectively. If the inductance is negligible, we obtain

$$I\,\frac{d^2\theta}{dt^2} + \left(k + \frac{G^2}{R}\right)\frac{d\theta}{dt} + c\theta = F(t) + \frac{G}{R}\,E(t). \quad (47)$$

It is assumed that the random couple is independent of that arising from the random e.m.f. in the coil so that $E(t)$ and $F(t)$ are uncorrelated. Hence (47) is of the same type as (33).

We can study (43), (44) and (47) by assuming that $\lambda_1$, $\lambda_2$ and $\kappa$ are constants. Note that the procedure adopted in the Appendix is not necessary. If $-a_1$ and $-a_2$ are the roots of the equation

$$X^2 + \lambda_1 X + \lambda_2 = 0, \tag{48}$$

then

$$Y = \frac{\kappa}{a_1 - a_2} \int_0^t X(\tau)\,(e^{-a_1(t-\tau)} - e^{-a_2(t-\tau)})\,d\tau. \tag{49}$$

The real parts of $a_1$, $a_2$ are all positive in the physical examples considered above. (Otherwise the differential equation would imply instability).

The moments of Y can be obtained by the same technique as we have adopted before. In this case, it is not possible to obtain an explicit expression for the $n$-th moment. Nevertheless the first few moments can always be obtained without much difficulty and we give below the second and third moments.

$$E\{Y^2\} = \Big[E\{Y\}\Big]^2 + \frac{\kappa^2}{a}\,\frac{E\{X^2\} - [E\{X\}]^2}{\lambda_2 \lambda_1}, \tag{50}$$

$$E\{Y^3\} = \Big[E\{Y\}\Big]^3 + 3\kappa^2 E\{Y\}\,\frac{E\{X^2\} - [E\{X\}]^2}{a\lambda_2\lambda_1}$$

$$= [E\{Y\}]^3 + 3E\{Y\}(E\{Y^2\} - [E\{Y\}]^2). \tag{51}$$

To obtain the correlation function of Y of degree two we write $a_1 = \xi + i\eta$, $a_2 = \xi - i\eta$, $\xi$ being positive. Then (49) becomes

$$Y(t) = \frac{1}{\eta} \int_0^t X(\tau)\, e^{-\xi(t-\tau)} \sin \eta(t-\tau)\, d\tau. \tag{52}$$

We wish to obtain $E\{Y(t_1)\,Y(t_2)\}$ when $t_1 \to \infty$ and $t_2 \to \infty$ in such a manner that $t_2 - t_1 =$ a constant $\equiv b$.

$E\{Y(t_1)\,Y(t_2)\}$ is given by

$$E\{Y(t_1)\,Y(t_2)\} = \frac{1}{\eta^2} \int_0^{t_1} \int_0^{t_2} e^{-\xi\{(t_1-\tau_1)+(t_2-\tau_2)\}} \sin \eta(t_1 - \tau_1)$$

$$\sin \eta(t_2 - \tau_2)\, E\{X(\tau_1)\,X(\tau_2)\}\, d\tau_1 d\tau_2. \tag{53}$$

Ramakrishnan (1954 *a*) has shown that

$$\mathrm{E}\{\mathrm{X}(\tau_1)\,\mathrm{X}(\tau_2)\} = [\mathrm{E}\{\mathrm{X}\}]^2\left[1 - \frac{1}{a_1}\,\delta(|\,\tau_2 - \tau_1\,|)\right] + \frac{1}{a}\,\mathrm{E}\{\mathrm{X}^2\}\,\delta(|\,\tau_2 - \tau_1\,|). \tag{54}$$

[This is indeed an immediate deduction from (28)]. If we now denote the R.H.S. of (54) by R ( $|\,\tau_2 - \tau_1\,|$ ) and introduce it into the R.H.S. of (53), the double integral can be reduced to a single integral (see Appendix B), and we have,

$$\lim_{\substack{t_1\to\infty,\ t_2\to\infty \\ t_2 - t_1 = b}} \mathrm{E}\{\mathrm{Y}(t_1)\,\mathrm{Y}(t_2)\} = \frac{1}{\xi\eta\sqrt{\xi^2+\eta^2}} \int_{-\infty}^{\infty} \mathrm{R}(b-\tau)\, e^{-\xi|\tau|} \sin\left(\eta\,|\,\tau\,| + \tan^{-1}\frac{\eta}{\xi}\right) d\tau. \tag{55}$$

Using the expression (54) for R, we obtain

$$\lim \mathrm{E}\{\mathrm{Y}(t_1)\,\mathrm{Y}(t_2)\} = \frac{\mathrm{E}\{\mathrm{X}^2\} - [\mathrm{E}\{\mathrm{X}\}]^2}{a\,\xi\eta\,(\xi^2+\eta^2)}\, e^{-\xi b}\ \ (\eta\cos b\eta + \xi\sin b\eta), \tag{56}$$

a result obtained by Wang and Uhlenbeck using spectral theory.

### LINEAR DIFFERENTIAL EQUATION OF *m*-TH ORDER

We shall finally consider the *m*-th order differential equation given by (1). We shall be concerned with the case where the solution is given by (2). When $\mathrm{X}(t) = dn(t)/dt$ explicit Laplace Transform solution of the p.f.f. of Y has been obtained by the authors. Note that the R.H.S. of (2) can be telescoped into a single integral so that (2) becomes

$$\mathrm{Y} = \phi_m(t) \int_0^t \phi_0(t_0)\,\kappa(t_0)\,\mathrm{X}(t_0)\, f(t, t_0)\, dt_0, \tag{57}$$

where

$$f(t, t_0) = \int_{t_0}^{t} \phi_1(t_1)\, dt_1 \int_{t_1}^{t} \phi_2(t_2)\, dt_2 \ldots \int_{t_{m-2}}^{t} \phi_{m-1}(t_{m-1})\, dt_{m-1}. \tag{58}$$

Written in this form, it is quite easy to see how the problem of obtaining the moments of Y could be dealt with. A formal expression for the *n*-th

moment of Y is given by

$$\mathrm{E}\{\mathrm{Y}^n\} = [\phi_m(t)]^n \int_0^t \int_0^t \ldots \int_0^t \phi_0(\tau_1)\,\phi_0(\tau_2)\ldots\phi_0(\tau_n)\,\kappa(\tau_1)\,\kappa(\tau_2)\ldots$$

$$\ldots\kappa(\tau_n)\,f(t,\tau_1)\,f(t,\tau_2)\ldots f(t,\tau_n)\,\mathrm{E}\{\mathrm{X}(\tau_1)\,\mathrm{X}(\tau_2)\ldots\mathrm{X}(\tau_n)\}$$

$$d\tau_1\,d\tau_2\ldots d\tau_n. \qquad (59)$$

In the theory of servo-mechanisms, the output Y and the input X are related by (2). If the input is *white noise*, *i.e.*, F.D.F. (as is usually the case) the moments of Y can be readily obtained. Jones and McCombie have recently discussed the Brownian fluctuation of galvanometers and galvanometer amplifiers. These processes are represented by differential equations of the type (1) and order higher than two. All the results of Jones and McCombie are capable of extension by the present method of approach.

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## APPENDIX A

Our object is to resolve the L.H.S. of (33) into operational factors. We make the transformation

$$Y = Z\, e^{-\frac{1}{2}\mu(t)} \tag{A-1}$$

where $\mu(t) = \int_0^t \lambda_1(\tau)\, d\tau$, (33) becomes

$$\frac{d^2z}{dt^2} + P(t)\, z = \kappa(t)\, X(t), \tag{A-2}$$

where $P(t)$ is given by

$$P(t) = -\frac{1}{4}\left[\lambda_1(t)\right]^2 - \frac{1}{2}\frac{d\lambda_1(t)}{dt} + \lambda_2(t). \tag{A-3}$$

Next we use the identity

$$\left[\frac{d}{dt} - \alpha_1(t)\right]\left[\frac{d}{dt} + \alpha_1(t)\right] z$$

$$\equiv \frac{d^2Z}{dt^2} + Z\{\alpha_1'(t) - [\alpha_1(t)]^2\}. \tag{A-4}$$

Hence if $\alpha_1$ is a solution of the Riccati equation

$$\frac{d\alpha}{dt} - \alpha^2 = P(t), \tag{A-5}$$

we can rewrite (A-2) as

$$\left[\frac{d}{dt} - \alpha_1(t)\right]\left[\frac{d}{dt} + \alpha_1(t)\right] Z = \kappa(t)\, X(t). \tag{A-6}$$

The solution is therefore given by

$$Z = \int_0^t e^{-\alpha_2(t)+\alpha_2(\tau)}\, d\tau \int_0^\tau e^{+\{\alpha_2(\tau)-\alpha_2(\tau')\}}\, \kappa(\tau')\, X(\tau')\, d\tau' \tag{A-7}$$

under proper initial conditions. Thus Y is given by

$$Y = e^{-\frac{1}{2}\mu(t)} \int_0^t e^{-\alpha_2(t)+\alpha_2(\tau)}\, d\tau \int_0^\tau e^{+\{\alpha_2(\tau)-\alpha_2(\tau')\}}\, \kappa(\tau')\, X(\tau')\, d\tau'. \tag{A-8}$$

In equations (A-7) and (A-8) above, $\alpha_2(t) = \int_0^t \alpha_1(\tau)\, d\tau$.

## APPENDIX B

We wish to reduce the R.H.S. of (53) to a single integral when $t_1 \to \infty$ and $t_2 \to \infty$ in such a manner that $t_2 - t_1 =$ a constant $= b$. For finite $\tau_1$ and $\tau_2$, $e^{-\xi\{(t_1-\tau_1)+(t_2-\tau_2)\}}$ tends to zero as $t_1$ and $t_2$ tend to infinity, and hence the whole contribution to the integral comes from values of $\tau_1$ and $\tau_2$ for which $t_1 - \tau_1 + t_2 - \tau_2$ is finite as $t_1, t_2 \to \infty$. The integral can be split up into two parts, in one of which $\tau_2 > \tau_1$, while in the other $\tau_2 < \tau_1$. We then obtain,

$$\mathrm{E}\{\mathrm{Y}(t_1)\,\mathrm{Y}(t_2)\} = \mathrm{A} + \mathrm{B} \tag{B-1}$$

where

$$\mathrm{A} = \frac{\kappa^2}{\eta^2} \int_0^{t_1} d\tau_1 \int_{\tau_1}^{t_2} e^{-\xi\,(t_1-\tau_1+t_2-\tau_2)} \sin\eta\,(t_1-\tau_1) \sin\eta\,(t_2-\tau_2)\,\mathrm{R}\,(\tau_2-\tau_1)\,d\tau_2 \tag{B-2}$$

and

$$\mathrm{B} = \frac{\kappa^2}{\eta^2} \int_0^{t_1} d\tau_2 \int_{\tau_2}^{t_1} e^{-\xi\,(t_1-\tau_1+t_2-\tau_2)} \sin\eta\,(t_1-\tau_1) \sin\eta\,(t_2-\tau_2)\,\mathrm{R}\,(\tau_1-\tau_2)\,d\tau_1 \tag{B-3}$$

These double integrals can be reduced to single integrals by changing the order of integration. We can then write A as

$$\mathrm{A} = \tfrac{1}{2}\int_0^b d\tau \int_0^{t_1} e^{-\xi\,(t_1+\tau_2-2\tau_1-\tau)}\,\mathrm{R}\,(\tau)[\cos\eta\,(\tau-b) - \cos\eta\,(t_1+t_2-2\tau_1-\tau)]\,d\tau_1 + \tfrac{1}{2}\int_b^{t_2} d\tau \int_0^{t_2-\tau} e^{-\xi(t_1+t_2-2\tau_1-\tau)}\,\mathrm{R}\,(\tau)\,[\cos\eta\,(\tau-b) - \cos\eta\,(t_1+t_2-2\tau_1-\tau)]\,d\tau. \tag{B-4}$$

Performing the integration we obtain,

$$\mathrm{A} = \frac{1}{2}\int_0^b \mathrm{R}\,(\tau)\Big[\cos\eta\,(\tau-b)\cdot\frac{1}{2\xi}\{e^{-\xi\,(b-\tau)} - e^{-\xi\,(t_1+t_2-\tau)}\} - \frac{1}{4(\xi^2+\eta^2)}\,e^{-\xi\,(b-\tau)}\{2\xi\cos\eta\,(b-\tau) - 2\eta\sin\eta\,(t_1+t_2-\tau)\} + \frac{1}{4(\xi^2+\eta^2)}\,e^{-\xi\,(t_1+t_2-\tau)}\{2\xi\cos\eta\,(t_1+t_2-\tau) - 2\eta \sin\eta\,(t_1+t_2-\tau)\}\Big]\,d\tau$$

$$+\frac{1}{2}\int_{b}^{t_2} R(\tau)\left[\cos\eta(t-b)\cdot\frac{1}{2\xi}\{e^{-\xi(\tau-b)}-e^{-\xi(t_1+t_2-\tau)}\}\right.$$

$$-\frac{1}{4(\xi^2+\eta^2)}e^{-\xi(\tau-b)}\{2\xi\cos\eta(\tau-b)-2\eta\sin\eta(\tau-b)\}$$

$$+\frac{1}{4(\xi^2+\eta^2)}e^{-\xi(t_1+t_2-\tau)}\{2\xi\cos\eta(t_1+t_2-\tau)-2\eta$$

$$\left.\sin\eta(t_1+t_2-\tau)\}\right]d\tau. \quad \text{(B-5)}$$

Passing to the limit, we have

$$\lim A=\frac{\eta}{4\xi\sqrt{\xi^2+\eta^2}}\int_{0}^{b} R(\tau)\sin\left\{\eta(b-\tau)+\sin^{-1}\frac{\xi}{\sqrt{\xi^2+\eta^2}}\right\}$$

$$e^{-\xi(b-\tau)}\,d\tau$$

$$+\frac{\eta}{4\xi\sqrt{\xi^2+\eta^2}}\int_{b}^{\infty} R(\tau)\sin\left\{\eta(\tau-b)+\sin^{-1}\frac{\eta}{\sqrt{\xi^2+\eta^2}}\right\}$$

$$e^{-\xi(\tau-b)}\,d\tau. \quad \text{(B-6)}$$

Repeating the same process for B, we obtain

$$\lim B=\lim\frac{1}{2}\int_{0}^{t_1} R(\tau)\left[\cos\eta(b+\tau)\cdot\frac{1}{2\xi}\{e^{-\xi(b+\tau)}-e^{-\xi(t_1+t_2-\tau)}\}\right.$$

$$-\frac{1}{4(\xi^2+\eta^2)}e^{-\xi(b+\tau)}\{2\xi\cos\eta(b+\tau)-2\eta\sin\eta(b+\tau)\}$$

$$+\frac{1}{4(\xi^2+\eta^2)}e^{-\xi(t_1+t_2-\tau)}\{2\xi\cos\eta(t_1+t_2-\tau)-2\eta$$

$$\left.\sin(t_1+t_2-\tau)\}\right]d\tau$$

$$=\frac{\eta}{4\xi\sqrt{\xi^2+\eta^2}}\int_{0}^{\infty} R(\tau)\,e^{-\xi(b+\tau)}\sin\left\{\eta(b+\tau)\right.$$

$$\left.+\sin^{-1}\frac{\eta}{\sqrt{\xi^2+\eta^2}}\right\}d\tau. \quad \text{(B-7)}$$

Hence on adding (B-6) and (B-7), we have

$$\lim E\{Y(t_1)\,Y(t_2)\}=\frac{\kappa^2}{4\xi\eta\sqrt{\xi^2+\eta^2}}\int_{-\infty}^{+\infty} R(b-\tau)\,e^{-\xi|\tau|}$$

$$\sin\left\{\eta|\tau|+\sin^{-1}\frac{\eta}{\sqrt{\xi^2+\eta^2}}\right\}d\tau. \quad \text{(B-8)}$$

# STUDIES ON THE DEPENDENCE OF OPTICAL ACTIVITY ON CHEMICAL CONSTITUTION

## Part XLIII. The Rotatory Dispersion of *d*-Camphor-β-Sulphonyl-phenyl-, *o*-tolyl-, *m*-tolyl-, *p*-tolyl, α-naphthyl, and β-naphthyl-amides

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In this communication we describe the rotatory dispersions of phenyl, tolyl (*o*-, *m*-, and *p*-) and naphthyl (α-, and β-) derivations of *d*-camphor-β-sulphonylamide in seven solvents. The *dimorphic* forms of *d*-camphor-β-sulphonyl phenylamide, now isolated for the first time, have been studied and characterised. In an earlier paper by one of us[1], this phenomenon of dimorphism was not observed. We have, therefore, prepared the mixed melting point-composition diagrams of Roozeboom, based on phase rule, of these dimorphic forms of the *dextro* modification with its *dl*-isomeride.

### Nature of the Rotatory Dispersion

These compounds exhibit '*simple*' rotatory dispersion as the rotatory power can be expressed by Drude's *one-term* equation, $[\alpha]_{\lambda}^{35^\circ} = k/\lambda^2 - \lambda_0^2$, where '$k$' is the rotation constant and $\lambda_0^2$, the dispersion constant. The differences in the calculated (*c*) and observed (*o*) values of the rotatory power, which are of the nature of casual experimental errors, are omitted from Tables I–VI to economise space: out of 494 observations of rotatory power, 19 exactly agree with the calculated values, 365 agree within $\pm 0{\cdot}02^\circ$ of the observed angle of rotation, 92 within $\pm 0{\cdot}04^\circ$ and the remaining 18 observations within $\pm 0{\cdot}06^\circ$. The abovementioned cases in which the differences between the observed and the calculated values of the rotatory power fall within $0{\cdot}04^\circ$–$0{\cdot}06^\circ$ of the observed angle of rotation are for wavelengths in the blue and the blue-violet regions of the spectrum which are difficult to read. The values of $\lambda_0$, the '*characteristic*' wavelength, vary from 3210 Å to 2049 Å in different solvents.

The '*simple*' nature of the rotatory dispersion of these compounds was first established by plotting the reciprocal of specific rotation, $1/[\alpha]_{\lambda}$, against the squares of the wavelengths, $\lambda^2$, when straight lines were obtained. A few of these graphs are given in Fig. 1. But the abovementioned more stringent algebraic test, based on the one-term Drude's equation, was applied in all cases (Tables I–VI).

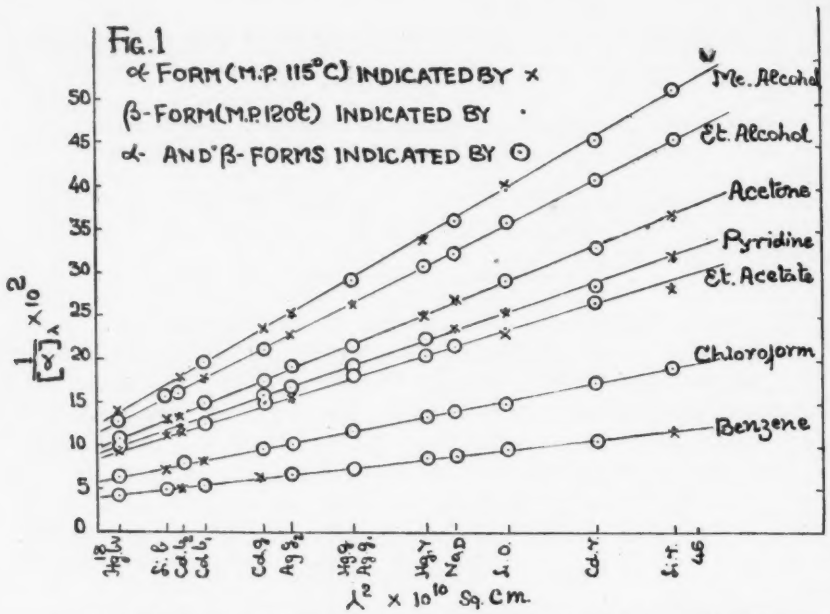



FIG. 1. The Rotatory Dispersion of α-Camphor-β-Sulphonyl phenylamides (dimorphic forms) in seven solvents.

## POSITION-ISOMERISM AND ROTATORY POWER

In Table A the sequence of the specific rotatory powers, $[\alpha]^{35°}_{5461}$, rotation constants, *ks*, and the '*characteristic*' wavelengths, $\lambda_0 s$, of *d*-camphor-β-sulphonyl-phenyl and tolyl (*o*-, *m*- and *p*-) amides in different solvents is given in the increasing order of their values:

TABLE A

| Solvent | $[\alpha]^{35°}_{5461}$ | *k* | $\lambda_0$ |
|---|---|---|---|
| Methyl alcohol | $un < m < p < o$ | $un < p < m < o$ | $o = m < p < un$ |
| Ethyl alcohol | $un < m < p < o$ | $un < m < p < o$ | $o < p < m < un$ |
| Acetone .. | $m < o < un < p$ | $m < un < p < o$ | $o < p = un < m$ |
| Pyridine .. | $o < m = p < un$ | $o < m < un < p$ | $p < un < m < o$ |
| Ethyl acetate .. | $o < m < un < p$ | $m < o < p < un$ | $o < un < p < m$ |
| Chloroform .. | $o < m < p < un$ | $o < m < p < un$ | $o < m < p < un$ |
| Benzene .. | $o < m < p < un$ | $o < m < p < un$ | $un < o < p < m$ |

TABLE I *a*

*The Rotatory Dispersion of* d*-Camphor-β-sulphonylphenylamide, α-form (m.p. 115° C.) in Different Solvents at 35° C.*

| Solvents | Methyl alcohol | | Ethyl alcohol | | Acetone | | Pyridine | | Ethyl acetate | | Chloroform | | Benzene | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Conc. in gm. per 100 c.c. | 1·0000 | | 1·0000 | | 1·0000 | | 1·0000 | | 1·0000 | | 1·0000 | | 1·0000 | |
| Calc. $[\alpha]_\lambda^{35°}$ | $\frac{7·292}{\lambda^2-0·088}$ | | $\frac{8·0275}{\lambda^2-0·087}$ | | $\frac{10·68}{\lambda^2-0·072}$ | | $\frac{11·245}{\lambda^2-0·084}$ | | $\frac{13·58}{\lambda^2-0·062}$ | | $\frac{20·4}{\lambda^2-0·065}$ | | $\frac{34·13}{\lambda^2-0·048}$ | |
| Calc. $\lambda_0$ Å | 2966 | | 2950 | | 2683 | | 2898 | | 2490 | | 2550 | | *2191* | |
| Lines | *o* | *c* | *o* | *c* | *o* | *c* | *o* | *c* | *o* | *c* | *o* | *c* | *o* | *c* |
| 6708 | +19·5° | +20·14° | +22·0° | +22·09° | +28·0° | +28·26° | +31·5° | +30·72° | +35·5° | +35·0° | +53·0° | +52·98° | +86·0° | +84·92° |
| 6438 | 22·0 | 22·32 | 24·5 | 24·51 | 30·0 | 31·19 | 34·5 | 34·02 | 37·0 | 38·53 | 58·5 | 58·37 | 95·0 | 93·13 |
| 6104 | 24·5 | 25·63 | 28·0 | 28·12 | 35·0 | 35·55 | 39·5 | 38·96 | 44·0 | 43·73 | 67·0 | 66·34 | 104·0 | 105·2 |
| 5893 | 28·0 | 28·13 | 31·0 | 30·85 | 39·0 | 38·82 | 42·5 | 42·72 | 47·5 | 47·62 | 73·0 | 72·30 | 113·0 | 114·1 |
| 5780 | 30·0 | 29·64 | 32·5 | 32·49 | 40·0 | 40·77 | 45·0 | 44·98 | 49·0 | 49·92 | 76·0 | 75·82 | 120·0 | 119·3 |
| 5468 | 34·5 | 34·55 | 38·0 | 37·87 | 47·0 | 47·06 | 52·5 | 52·30 | 56·0 | 57·31 | 87·0 | 87·18 | 135·0 | 136·0 |
| 5461 | 34·5 | 34·69 | 38·0 | 38·02 | 47·0 | 47·22 | 53·0 | 52·49 | 56·5 | 57·49 | 87·5 | 87·48 | 135·5 | 136·5 |
| 5209 | 40·0 | 39·77 | 43·5 | 43·56 | 53·5 | 53·58 | 60·0 | 60·03 | 63·0 | 64·89 | 100·0 | 98·88 | 152·5 | 152·9 |
| 5086 | 42·5 | 42·75 | 47·0 | 46·78 | 58·0 | 57·24 | 64·0 | 64·40 | 68·0 | 69·07 | 105·5 | 105·4 | 161·5 | 162·1 |
| 4800 | 51·5 | 51·21 | 56·0 | 55·99 | 66·5 | 67·42 | 75·5 | 76·79 | 80·0 | 80·61 | 123·0 | 123·3 | 187·5 | 187·2 |
| 4678 | 56·0 | 55·76 | 62·5 | 60·91 | 73·0 | 72·74 | 81·5 | 83·41 | 86·5 | 86·62 | 131·0 | 132·6 | 201·5 | 199·9 |
| 4603 | 59·0 | 58·89 | 65·5 | 64·33 | 77·0 | 76·38 | 89·0 | 87·96 | 91·5 | 90·67 | 141·0 | 139·0 | 210·0 | 208·4 |
| 4358 | 72·0 | 71·48 | 78·0 | 78·0 | 91·5 | 90·51 | 104·5 | 106·00 | 108·0 | 106·1 | 162·5 | 163·2 | 242·0 | 240·7 |

## TABLE I *b*

*The Rotatory Dispersion of* d*-Camphor-β-sulphonylphenylamide, β-form (m.p. 120° C.) in Different Solvents at 35° C.*

| Solvents | Methyl alcohol | | Ethyl alcohol | | Acetone | | Pyridine | | Ethyl acetate | | Chloroform | | Benzene | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Conc. in gm. per 100 c.c. | 1·000 | | 1·000 | | 1·000 | | 1·000 | | 1·000 | | 1·000 | | 1·000 | |
| Calc. $[\alpha]_\lambda^{35°}$ | $\frac{7·292}{\lambda^2-0·088}$ | | $\frac{8·0275}{\lambda^2-0·087}$ | | $\frac{10·68}{\lambda^2-0·072}$ | | $\frac{11·245}{\lambda^2-0·084}$ | | $\frac{13·58}{\lambda^2-0·062}$ | | $\frac{20·4}{\lambda^2-0·065}$ | | $\frac{34·13}{\lambda^2-0·048}$ | |
| Calc. $\lambda_0$ Å | 2966 | | 2950 | | 2683 | | 2898 | | 2490 | | 2550 | | *2191* | |
| Lines | *o* | *c* | *o* | *c* | *o* | *c* | *o* | *c* | *o* | *c* | *o* | *c* | *o* | *c* |
| 6708 | +19·5° | +20·14° | +22·0° | +22·09° | +27·5° | +28·26° | +32·0° | +30·72° | +35·0° | +35·00° | +53·0° | +52·98° | +84·0° | +84·92° |
| 6438 | 22·0 | 22·32 | 24·5 | 24·51 | 30·0 | 31·19 | 35·0 | 34·02 | 37·5 | 38·53 | 58·0 | 58·37 | 96·0 | 93·13 |
| 6104 | 25·5 | 25·63 | 28·0 | 28·12 | 34·5 | 35·55 | 40·0 | 38·96 | 42·5 | 43·73 | 67·5 | 66·34 | 104·5 | 105·2 |
| 5893 | 28·0 | 28·13 | 31·0 | 30·85 | 38·0 | 38·82 | 43·0 | 42·72 | 47·0 | 47·62 | 73·0 | 72·30 | 114·0 | 114·1 |
| 5780 | 29·5 | 29·64 | 32·5 | 32·49 | 39·5 | 40·77 | 45·0 | 44·98 | 49·0 | 49·92 | 76·5 | 75·82 | 120·0 | 119·3 |
| 5468 | 34·5 | 34·55 | 37·0 | 37·87 | 47·0 | 47·06 | 52·5 | 52·30 | 55·5 | 57·31 | 87·0 | 87·18 | 135·0 | 136·0 |
| 5461 | 34·5 | 34·69 | 37·5 | 38·02 | 47·0 | 47·22 | 53·0 | 52·49 | 56·0 | 57·49 | 87·0 | 87·48 | 135·0 | 136·5 |
| 5209 | 40·5 | 39·77 | 43·0 | 43·56 | 52·5 | 53·58 | 60·0 | 60·03 | 65·0 | 64·89 | 100·0 | 98·88 | 153·0 | 152·9 |
| 5086 | 43·0 | 42·75 | 47·5 | 46·78 | 57·5 | 57·24 | 64·0 | 64·4 | 68·0 | 69·07 | 105·0 | 105·4 | 164·0 | 162·1 |
| 4800 | 51·0 | 51·21 | 57·0 | 55·99 | 66·5 | 67·42 | 74·5 | 76·71 | 80·0 | 80·61 | 120·0 | 123·3 | 186·5 | 187·2 |
| 4678 | 57·5 | 55·76 | 63·0 | 60·91 | 74·5 | 72·74 | 82·0 | 83·41 | 85·0 | 86·62 | 131·5 | 132·5 | 203·0 | 199·9 |
| 4603 | 60·0 | 58·89 | 65·5 | 64·33 | 77·5 | 76·38 | 86·5 | 87·96 | 91·0 | 90·67 | 138·0 | 139·0 | 209·5 | 208·4 |
| 4358 | 73·0 | 71·48 | 78·0 | 77·76 | 92·0 | 90·51 | 103·0 | 106·0 | 103·5 | 106·1 | 162·5 | 163·2 | 243·0 | 240·7 |

## TABLE II

*The Rotatory Dispersion of* d*-Camphor-β-sulphonyl-*o*-tolylamide, m.p.* 110° *C. in Different Solvents at* 35° *C.*

| Solvents | Methyl alcohol | | Ethyl alcohol | | Acetone | | Pyridine | | Ethyl acetate | | Chloroform | | Benzene | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Conc. in gm. per 100 c.c. | 1·000 | | 1·000 | | 1·000 | | 1·000 | | 1·000 | | 1·000 | | 1·000 | |
| Calc. $[\alpha]_\lambda^{35°}$ | $\frac{8·835}{\lambda^2-0·078}$ | | $\frac{10·1}{\lambda^2-0·062}$ | | $\frac{11·177}{\lambda^2-0·058}$ | | $\frac{9·1624}{\lambda^2-0·0976}$ | | $\frac{12·62}{\lambda^2-0·042}$ | | $\frac{14·506}{\lambda^2-0·042}$ | | $\frac{20·611}{\lambda^2-0·0484}$ | |
| Calc. $\lambda_0$ Å | 2793 | | 2490 | | 2408 | | 3123 | | *2049* | | *2049* | | *2200* | |
| Lines | *o* | *c* | *o* | *c* | *o* | *c* | *o* | *c* | *o* | *c* | *o* | *c* | *o* | *c* |
| 6708 | +23·5° | +23·75° | +26·0° | +26·03° | +28·5° | +28·5° | +26·0° | +26·0° | +31·0° | +30·93° | +36·0° | +35·55° | +51·0° | +51·34° |
| 6438 | 26·0 | 26·26 | 28·5 | 28·65 | 31·0 | 31·34 | 29·0 | 28·92 | 34·0 | 33·88 | 39·0 | 38·94 | 56·0 | 56·30 |
| 6104 | 30·0 | 30·00 | 32·5 | 32·53 | 36·0 | 35·53 | 33·5 | 33·33 | 38·5 | 38·19 | 45·0 | 43·89 | 63·5 | 63·6 |
| 5893 | 32·5 | 32·82 | 35·0 | 35·42 | 38·5 | 38·64 | 37·0 | 36·70 | 41·5 | 41·35 | 47·5 | 47·52 | 69·0 | 69·0 |
| 5780 | 34·5 | 34·51 | 37·0 | 37·13 | 40·5 | 40·49 | 38·5 | 38·77 | 43·5 | 43·22 | 50·0 | 49·62 | 73·0 | 72·18 |
| 5468 | 40·0 | 39·97 | 43·0 | 42·62 | 45·5 | 46·36 | 45·5 | 45·5 | 49·5 | 49·15 | 56·5 | 56·44 | 83·5 | 82·26 |
| 5461 | 40·0 | 40·13 | 43·0 | 42·76 | 46·0 | 46·51 | 46·0 | 45·67 | 50·0 | 49·27 | 57·0 | 56·62 | 83·5 | 82·50 |
| 5209 | 45·5 | 45·69 | 48·5 | 48·26 | 52·5 | 52·38 | 53·0 | 52·76 | 54·5 | 55·04 | 63·0 | 63·25 | 93·0 | 92·9 |
| 5086 | 49·0 | 48·93 | 52·0 | 51·37 | 55·5 | 55·71 | 56·0 | 56·92 | 58·5 | 58·26 | 65·5 | 66·95 | 97·5 | 97·83 |
| 4800 | 58·0 | 57·98 | 60·0 | 59·96 | 65·5 | 64·82 | 69·0 | 69·0 | 67·0 | 66·9 | 77·0 | 76·89 | 113·0 | 113·2 |
| 4678 | 62·5 | 62·76 | 66·0 | 64·42 | 71·0 | 69·5 | 75·0 | 75·60 | 71·0 | 71·39 | 83·5 | 82·04 | 121·0 | 121·0 |
| 4603 | 66·5 | 66·03 | 68·5 | 67·41 | 73·0 | 72·66 | 82·5 | 80·23 | 75·0 | 74·32 | 86·5 | 85·41 | 128·0 | 126·1 |
| 4358 | 80·5 | 78·89 | 81·0 | 78·72 | 86·0 | 84·65 | 100·0 | 99·26 | 86·5 | 85·33 | 97·5 | 98·06 | 148·0 | 145·6 |

## TABLE III

*The Rotatory Dispersion of* d*-Camphor-β-sulphonyl-*m*-tolylamide, m.p.* 100° *C. in Different Solvents at* 35° *C.*

| Solvents | Methyl alcohol | | Ethyl alcohol | | Acetone | | Pyridine | | Ethyl acetate | | Chloroform | | Benzene | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Conc. in gm. per 100 c.c. | 1·000 | | 1·000 | | 1·000 | | 1·000 | | 1·000 | | 1·000 | | 1·000 | |
| Calc. $[\alpha]_{\lambda}^{35°}$ | $\frac{8·028}{\lambda^2-0·078}$ | | $\frac{8·31}{\lambda^2-0·082}$ | | $\frac{8·9}{\lambda^2-0·094}$ | | $\frac{10·95}{\lambda^2-0·085}$ | | $\frac{11·47}{\lambda^2-0·080}$ | | $\frac{19·909}{\lambda^2-0·0557}$ | | $\frac{31·76}{\lambda^2-0·053}$ | |
| Calc. $\lambda_0$ Å | 2793 | | 2864 | | 3066 | | 2915 | | 2828 | | *2359* | | *2302* | |
| Lines | *o* | *c* | *o* | *c* | *o* | *c* | *o* | *c* | *o* | *c* | *o* | *c* | *o* | *c* |
| 6708 | +21·5° | +21·58° | +22·5° | +22·58° | +25·0° | +25·0° | +30·0° | +30·00° | +31·0° | +30·99° | +51·0° | +50·51° | +80·0° | +80·00° |
| 6438 | 23·5 | 23·86 | 25·0 | 25·00 | 28·0 | 27·77 | 33·5 | 33·24 | 34·5 | 34·30 | 55·5 | 55·49 | 87·5 | 87·1 |
| 6104 | 27·0 | 27·27 | 28·5 | 28·61 | 32·5 | 31·96 | 38·5 | 38·09 | 39·5 | 39·21 | 63·5 | 62·85 | 100·0 | 99·4 |
| 5893 | 29·5 | 29·82 | 31·0 | 31·34 | 35·5 | 34·88 | 42·5 | 41·77 | 43·0 | 42·95 | 68·0 | 68·31 | 107·5 | 108·0 |
| 5780 | 31·5 | 31·36 | 33·0 | 32·98 | 37·0 | 37·09 | 44·0 | 43·98 | 45·5 | 45·05 | 72·0 | 71·55 | 114·0 | 113·1 |
| 5468 | 36·5 | 36·33 | 38·0 | 38·29 | 44·0 | 43·41 | 51·5 | 51·18 | 53·5 | 52·38 | 82·0 | 81·85 | 129·0 | 129·1 |
| 5461 | 36·5 | 36·46 | 38·5 | 38·41 | 44·5 | 43·61 | 52·0 | 51·41 | 53·5 | 52·55 | 82·0 | 82·12 | 130·0 | 129·5 |
| 5209 | 41·5 | 41·53 | 43·5 | 43·89 | 50·0 | 50·20 | 59·0 | 58·79 | 60·0 | 59·95 | 92·0 | 92·37 | 146·0 | 145·4 |
| 5086 | 44·0 | 44·45 | 47·0 | 47·06 | 55·0 | 54·08 | 63·0 | 63·10 | 64·0 | 64·21 | 98·5 | 98·13 | 154·0 | 154·5 |
| 4800 | 51·5 | 52·09 | 56·0 | 55·99 | 66·0 | 65·16 | 73·5 | 75·32 | 76·5 | 76·26 | 114·5 | 114·0 | 178·5 | 178·9 |
| 4678 | 55·5 | 57·03 | 60·0 | 60·74 | 70·0 | 71·02 | 80·5 | 81·85 | 83·5 | 82·6 | 122·5 | 122·1 | 190·0 | 191·5 |
| 4603 | 60·0 | 59·99 | 65·0 | 64·00 | 76·5 | 75·54 | 86·0 | 86·36 | 89·5 | 87·02 | 130·0 | 127·6 | 200·0 | 200·0 |
| 4358 | 71·0 | 71·68 | 77·0 | 76·95 | 93·0 | 92·81 | 104·5 | 104·3 | 105·0 | 104·4 | 149·0 | 148·3 | 233·0 | 233·5 |

## TABLE IV

*The Rotatory Dispersion of* d-*Camphor-β-sulphonyl-*p-*tolylamide, m.p.* 141° *C. in Different Solvents at* 35° *C.*

| Solvents | Methyl alcohol | | Ethyl alcohol | | Acetone | | Pyridine | | Ethyl acetate | | Chloroform | | Benzene | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Conc. in gm. per 100 c.c. | 1·000 | | 1·000 | | 1·000 | | 1·000 | | 1·000 | | 1·000 | | 1·000 | |
| Calc. $[\alpha]_\lambda^{35°}$ | $\frac{7·9296}{\lambda^2-0·0841}$ | | $\frac{8·57}{\lambda^2-0·077}$ | | $\frac{10·77}{\lambda^2-0·072}$ | | $\frac{11·29}{\lambda^2-0·080}$ | | $\frac{13·54}{\lambda^2-0·076}$ | | $\frac{20·137}{\lambda^2-0·059}$ | | $\frac{32·78}{\lambda^2-0·0503}$ | |
| Calc. $\lambda_0$ Å | 2898 | | 2775 | | 2683 | | 2828 | | 2757 | | *2429* | | *2243* | |
| Lines | *o* | *c* | *o* | *c* | *o* | *c* | *o* | *c* | *o* | *c* | *o* | *c* | *o* | *c* |
| 6708 | +22·0° | +21·67° | +23·0° | +23·04° | +28·5° | +28·49° | +30·5° | +30·5° | +36·5° | +36·33° | +51·5° | +51·48° | +82·0° | +82·0° |
| 6438 | 24·0 | 24·0 | 25·5 | 25·4 | 31·5 | 31·46 | 34·0 | 33·75 | 40·0 | 40·13 | 56·5 | 56·63 | 90·0 | 90·01 |
| 6104 | 27·5 | 27·49 | 29·0 | 29·0 | 36·0 | 35·85 | 38·5 | 38·55 | 45·5 | 45·7 | 64·5 | 64·22 | 102·5 | 101·7 |
| 5893 | 30·0 | 30·13 | 31·5 | 31·72 | 39·0 | 39·14 | 42·0 | 42·25 | 50·5 | 49·82 | 70·0 | 69·85 | 110·0 | 110·4 |
| 5780 | 32·0 | 31·76 | 33·0 | 33·42 | 41·5 | 41·11 | 44·5 | 44·36 | 52·5 | 52·52 | 74·0 | 73·21 | 116·0 | 115·5 |
| 5468 | 37·0 | 36·90 | 38·5 | 38·55 | 47·5 | 47·45 | 52·0 | 51·54 | 60·0 | 60·74 | 84·0 | 83·89 | 131·5 | 131·8 |
| 5461 | 37·0 | 37·03 | 39·0 | 38·73 | 47·5 | 47·62 | 52·0 | 51·74 | 60·5 | 60·95 | 84·0 | 84·26 | 132·0 | 132·2 |
| 5209 | 42·0 | 42·35 | 44·0 | 44·11 | 53·5 | 54·03 | 58·5 | 59·01 | 69·0 | 69·34 | 96·0 | 94·84 | 147·0 | 148·0 |
| 5086 | 45·0 | 45·44 | 47·0 | 47·09 | 57·5 | 57·73 | 63·5 | 63·20 | 74·0 | 74·20 | 101·9 | 100·0 | 156·0 | 157·3 |
| 4800 | 54·0 | 54·19 | 56·0 | 55·76 | 68·0 | 68·0 | 75·5 | 75·06 | 88·0 | 87·7 | 117·5 | 117·4 | 183·5 | 182·0 |
| 4678 | 59·0 | 58·86 | 61·0 | 60·45 | 73·0 | 73·36 | 82·5 | 81·30 | 95·0 | 94·88 | 128·5 | 126·0 | 196·0 | 194·5 |
| 4603 | 61·5 | 62·90 | 64·5 | 63·72 | 77·5 | 76·96 | 87·0 | 85·67 | 100·0 | 99·77 | 133·0 | 131·8 | 204·5 | 203·0 |
| 4358 | 73·0 | 74·87 | 77·0 | 75·86 | 90·0 | 91·28 | 104·0 | 102·6 | 116·5 | 118·9 | 154·0 | 153·3 | 237·0 | 234·6 |

We find that Frankland's *lever-arm hypothesis*[2] and its *electrostatic* modification of Rule,[3] according to both of which the *meta* isomeride should be intermediate between the *ortho* and the *para* isomers, while the *unsubstituted* (*un*) compound should be equal to or less than the *ortho* compound as regards the rotatory power, is partially followed in pyridine, chloroform and benzene but not even in a single case in the other four solvents. On the other hand Cohen's *rule*[4] which states that the rotatory power produced by an *ortho* substituent differs more from that of the unsubstituted compound than do those of *meta* and *para* isomerides, is obeyed in all solvents except the *meta* isomeride in acetone (Tables I–IV).

In the abovementioned comparisons, the specific rotatory powers (Table A) for mercury green line ($\lambda = 5461$ Å) are used. The results obtained for this line do not hold good, however, for other wavelengths: for instance, for mercury blue-violet line ($\lambda = 4358$ Å), the sequences are the same in ethyl acetate, chloroform and benzene but not in the remaining four solvents. It is thus evident that there is no generalisation correlating the esoteric property of optical activity with different parameters.

The sequence of the ' rotation constants ', ' *ks* ', in the increasing order of their values is the same as that of the specific rotatory powers, $[\alpha]_{5461}^{35°}$ in ethyl alcohol, chloroform and benzene but not in the remaining four solvents (Table A).

The sequence, of the decreasing values of the ' *characteristic* ' wavelengths, $\lambda_0 s$, for the different position isomerides does not run parallel to that of the other two constants, namely, specific rotatory power, $[\alpha]_{5461}^{35°}$, and the rotation constant, ' *k* ' (Table A). Generally it also varies in different solvents.

## INFLUENCE OF SOLVENT ON ROTATORY POWER

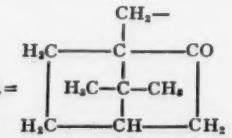
Table B gives the specific rotatory powers, $[\alpha]_{5461}^{35°}$, and rotation constants, *ks*, of *d*-camphor-$\beta$-sulphonyl-phenyl, tolyl (*o*-, *m*- and *p*-) and naphthyl ($\alpha$- and $\beta$-) amides. It is found that the specific rotatory powers in different solvents increase with the decreasing value of the dielectric constants of the solvents. The same is the case with the rotation constant, *ks*, except in the case of *d*-camphor-$\beta$-sulphonyl-*o*-tolylamide, where the magnitude of the rotation constant in pyridine (9·16) is lower than that in ethyl alcohol (10·1) and acetone (11·18).

TABLE B

*Specific Rotatory Powers for* $Hg_{5461}$ *at 35° C. in Different Solvents*

| Structural formula† | MeOH [31·5]* | EtOH [25·8] | Acetone [21·5] | Pyridine [12·4] | EtOAc [6·11] | $CHCl_3$ [5·2] | $C_6H_6$ [2·28] |
|---|---|---|---|---|---|---|---|
| $R\text{–}SO_2NHC_6H_5$ .. | 34·5<br>‡(7·30) | 38·0<br>(8·03) | 47·0<br>(10·68) | 53·0<br>(11·25) | 56·5<br>(13·58) | 87·5<br>(20·4) | 135·5<br>(34·13) |
| $R\text{–}SO_2NHC_6H_4CH_3$ (*ortho*) .. | 40·0<br>(8·84) | 43·0<br>(10·1) | 46·0<br>(11·18) | 46·0<br>(9·16) | 50·0<br>(12·62) | 57·0<br>(14·50) | 83·0<br>(20·61) |
| $R\text{–}SO_2NHC_6H_4CH_3$ (*meta*) .. | 36·5<br>(80·3) | 38·5<br>(8·31) | 44·5<br>(8·9) | 52·0<br>(10·95) | 53·5<br>(11·47) | 82·0<br>(19·91) | 130·0<br>(31·76) |
| $R\text{–}SO_2NHC_6H_4CH_3$ (*para*) .. | 37·0<br>(7·93) | 39·0<br>(8·57) | 47·5<br>(10·77) | 52·0<br>(11·29) | 60·5<br>(13·54) | 84·0<br>(20·14) | 132·0<br>(32·78) |
| $R\text{–}SO_2NHC_{10}H_7$ ($\alpha$) .. | 43·0<br>(8·22) | 47·0<br>(10·39) | ..<br>.. | 51·5<br>(11·4) | ..<br>.. | ..<br>.. | 83·0<br>(20·45) |
| $R\text{–}SO_2NHC_{10}H_7$ ($\beta$) .. | 27·0<br>(5·67) | 29·75<br>(6·45) | 37·0<br>(8·53) | ..<br>.. | ..<br>.. | 97·5<br>(22·8) | 161·5<br>(37·3) |

† R =



* Figures in square brackets are the values of the dielectric constants of the solvent.

‡ The figures in simple brackets are the 'rotation constants', *ks*.

### '*Characteristic*' Wavelengths Derived from Dispersion Constants of Drude's Equations

The general rotatory dispersion equation of Drude, $[\alpha]_\lambda = \Sigma K/\lambda^2 - \lambda_0^2$, contains in the summation, several 'partial rotations' such as $k'/\lambda^2 - \lambda'_0{}^2$, $k''/\lambda^2 - \lambda''_0{}^2$, etc. with the '*characteristic*' wavelengths of the absorption bands, $\lambda_0'$, $\lambda_0''$, etc. in the ultra-violet region of the spectrum which govern the rotatory power of the optically active compound. The rotatory dispersion equation of camphor[5] is complex and can be expressed by the *two-term* Drude's equation:

$$[\alpha]_\lambda{}^{35^\circ} = \frac{29{\cdot}87}{\lambda^2 - 0{\cdot}0852} - \frac{19{\cdot}96}{\lambda^2 - 0{\cdot}0521} \quad \text{(Solvent—Benzene; Conc. 34·5\%)}$$

This equation contains the low frequency corresponding to $\lambda_0' = 2920$ Å, which is characteristic of the unsaturated ketonic group $> C = 0$, pertaining to the selective absorption band ($\lambda_{abs} = 2880$ Å) of camphor.[6] The high frequency corresponding to the '*characteristic*' wavelength $\lambda_0'' = 2283$ Å, pertains to general absorption of the saturated compounds. Similarly Reychler's camphor-$\beta$-sulphonic acid[7] in water exhibits complex rotatory dispersion containing the low frequency, corresponding to $\lambda_0' = 2918$ Å, and high frequency corresponding to $\lambda_0'' = 2223{\cdot}6$ Å. On the other hand the salts of the campor-$\beta$-sulphonic acid with inorganic bases and organic nitrogen bases show '*simple*' rotatory dispersion expressed by the *one-term* Drude's equation, $[\alpha]_\lambda = k/\lambda^2 - \lambda_0^2$, in which the term containing the high frequency has disappeared. There is only the term containing the low frequency of the ketonic group.[8]

In the compounds now described, the rotatory dispersion in all the solvents is '*simple*' as it can be expressed by the *one-term* Drude equation. The '*characteristic*' wavelengths, $\lambda_0$s, deduced from the dispersion equations vary from 3210 Å to 2049 Å. In solvents of *high* and *medium* dielectric constants, $\lambda_0$ varies from 3210 Å to 2408 Å. This corresponds to the ketonic absorption band abovementioned, which governs the rotatory power of the compounds. But in solvents of *low* dielectric constants, such as ethyl acetate (6·11), chloroform (5·2) and benzene (2·28), the values of $\lambda_0$ vary in several cases from 2429 Å to 2049 Å. They correspond to the general absorption of saturated molecules and are indicated in italics in Tables I to IV. As in previous work from this laboratory with (Miss) M. K. Parukutty Amma,[13] we are not yet able to offer any definite explanation of this change of $\lambda_0$ from the low frequency to the high frequency. This must, however, await confirmation by direct measurement of ultra-violet absorption of these com-

pounds for elucidating this surprising result in which the low frequency corresponding to the keto group of the compounds has been replaced by the high frequency corresponding to the saturated molecules.

## Dimorphic Forms

Polymorphism is a phenomenon of fairly common occurrence. It differs from isomerism, tautomerism and polymerism: if the difference is due to the chemical structure of the molecule, it is classed as isomerism (including tautomerism and polymerism). On the other hand if the difference is brought about by a different space lattice arrangement of identical molecules in the crystals, it is said to be polymorphism. One of the authors[9] has described a method, based on optical activity, for distinguishing isomeric, polymeric and tautomeric from polymorphic optically active substances. It depends on the following considerations: if the modifications form a single independent component, they are polymorphic. The differences between them will be confined to the solid state only. When once the crystal structure is broken down, they will disappear. On the other hand, if the modifications form as many independent components, they are isomeric. The difference between them will persist in solution, unless tautomeric equilibrium has been established. The methods which have been employed for ascertaining the polymorphic or isomeric (tautomeric) nature of the modifications depend on finding out whether the solutions given by them are identical or not. These methods will obviously fail in the case of the tautomeric substances with a large velocity of change as the solutions of the different modifications on account of tautomeric equilibrium will be identical. The tautomeric modifications will, therefore, appear as polymorphic.

Both Sidgwick[10] and Bruni[12] have also made use of the abovementioned properties of the solutions of the two classes of substances and devised a method of diagnosis depending on the solubility.

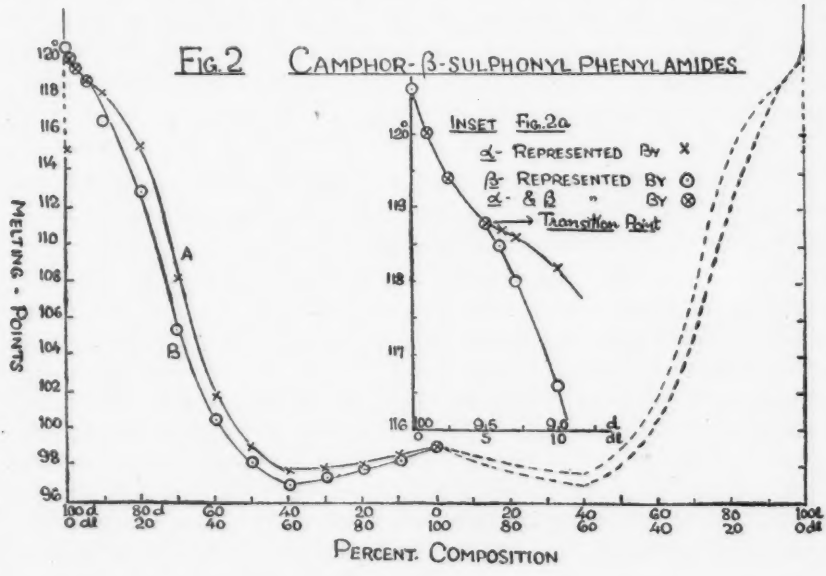
The study of the rotatory dispersion of solutions of polymorphic and isomeric modifications of optically active substances discussed above, furnishes a much simpler but equally trustworthy method of distinguishing between them. It thus follows that the rotatory power of each of the polymorphous modifications will be identical, whereas it will be different in the case of isomeric or tautomeric forms. We have employed this method for the diagnosis of the dimorphous forms of *d*-camphor-$\beta$-sulphonyl phenyl amide ($\alpha$-form, m.p. 115° C. and $\beta$-form, m.p. 120° C.). In Tables I *a* and I *b*, the rotatory dispersion of both forms ($\alpha$ and $\beta$) of *d*-camphor-$\beta$-sulphonyl phenylamide are given and are found to be identical within the limits of experimental errors. This is also shown in Fig. 1, where the straight lines

representing the rotatory dispersions of these two forms superpose on each other.

### ROOZEBOOM'S MIXED MELTING POINT-COMPOSITION DIAGRAMS FOR THE MIXTURES OF THE RACEMIC MODIFICATIONS WITH THEIR *d*- (OR *l*-) ISOMERIDES

Roozeboom has described two physical methods, based on phase rule, for determining the nature of the racemic modifications of the optically active forms: one of them consists in the preparation of freezing point-composition diagram for the mixture of the *dl*-form with its optically active isomeride. If the diagram is composed of *three* curves, it is a racemic compound; of *two* curves a racemic mixture and of *one* curve a racemic solid solution.

In a previous communication,[1] the abovementioned diagrams were prepared for these compounds and the nature of the racemic modification was discussed. With the discovery of the dimorphic forms of *d*-camphor-β-sulphonyl phenylamide above discussed, it was necessary to reinvestigate this problem with the aid of Roozeboom's diagrams: the mixed melting point-composition diagram of the α-form of *d*-camphor-β-sulphonyl phenylamide (m.p. 115° C.) with the racemic form (m.p. 99° C.) is very interesting (Fig. 2 A). Its general shape is similar to that of the β-form (Fig. 2 B) and



consists of three curves, establishing the racemic form to be a true *dl*-compound. The dotted portion of the curve, *dl-l*, is the mirror-image of the curve *d-dl*.

The melting point of the α-form (115° C.) and that of the β-form (m.p. 120·6°) with admixtures of 1, 2·5 and 5 per cent. of the *dl*-form are identical, namely, 120·0°, 119·4° and 118·8° C. respectively (*vide*, Table VII, Fig. 2); in other words, the mixed melting point-composition diagrams of α- and β-form with *dl*-form are superposable on each other in this range. With 6 and 7 per cent. admixtures of the *dl*-form with the α-form, the melting points of the mixtures are about 0·2° and 0·6° C. higher than those with the β-form respectively. With 10 per cent. admixture the melting points are, α-form, 118·4° and β-form 116·6°; with 20 per cent. admixture of *dl*-form, the melting point of α-form is 115·6° and of β-form, 112·6° C. and with 30 per cent. admixture of *dl*-form, they are 108·1° and 102·9° respectively. As the amount of the *dl*-isomeride in the mixture increases from 30 per cent. to 95 per cent., the difference in the melting points of mixtures of the α- and β-form with the *dl*-isomeride decreases from 2·9° to 0·1°; the melting points of the mixtures with the α-form being, however, always higher than those with the β-form, except for the composition range, zero per cent. *dl* to 5 per cent. *dl*, in which case the two curves are identical. The point at which the two curves meet is the transformation (transition) temperature of the α- into β-form. It is found to be 118·8° C. It is more clearly shown in the inset diagram (Fig. 2 *a*) drawn on a larger scale.

The α-form is the metastable form as it changes on heating into the β-form. According to Ostwald's rule, it has higher energy which is released when it is transformed into the *stable* β-modification.

The melting points of the mixtures of *dl*-form, with α-form (*metastable form*) are higher than those with β-form (*stable form*) except as indicated above. This is brought about by the greater energy associated with the α-form. The depression in the melting points of α-form, due to addition of different amounts of *dl*-form should have, according to freezing-point equation, caused the melting point curve of α-form to lie below that of the β-form, had there been no change of the α-form into the β-form. But since the α-form changes into the β-form under the experimental conditions, its melting point curve should have been identical with that of the β-form. The extra energy released during the transformation, however, raises the temperature of the melt of the mixture of the α-form with *dl*-form above that of the β-form with *dl*-form. Its curve, therefore, lies above that of the β-form. This holds if the transformation temperature is higher than the melting

points of the mixtures. If it is lower than the melting points of the mixtures, the two curves will be identical. Based on this principle a method has been devised to determine the temperature of transformation of the dimorphic forms as described in the following section.

### DETERMINATION OF TRANSFORMATION (TRANSITION) TEMPERATURE OF α- INTO β-FORM

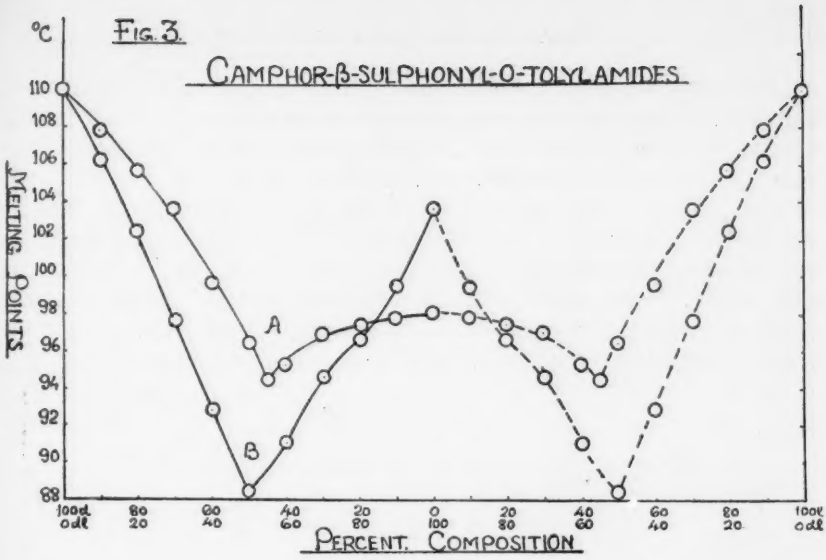
There are seven methods described by Findlay[11] for the determination of transformation (transition) temperature of dimorphic and polymorphic forms, namely, (*a*) Dilatometric method, (*b*) Vapour-pressure measurement method, (*c*) Solubility measurement method, (*d*) thermometric method, (*e*) Optical methods, (*f*) Electrical methods, and (*g*) Viscosity method.

We describe in this paper a very elegant and convenient method for the determination of transformation temperature, based on the melting point-composition diagrams of the metastable and stable forms with a third substance as described above. If the transition temperature is higher than the melting points of the mixtures, the curve of the *metastable* form (α) will always lie above that of the *stable* form (β). If however the transformation temperature is lower than the melting points of the mixtures, the melting point curve of α-form and the β-form with the *dl*-form will be identical. The point where the two curves meet will be the transformation temperature. By applying this method it is found that the transformation temperature of α- into β-form of *d*-camphor-β-sulphonyl phenylamide is 118·8° C. (Fig. 2; Inset Fig. 2 *a* drawn on a larger scale).

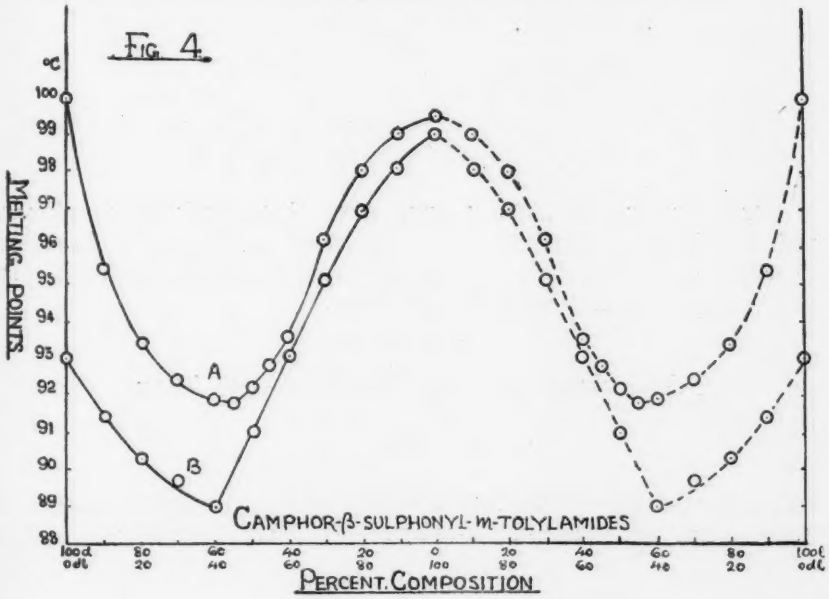
*m*-Chlorophenylamino-*dl*-camphor which also occurs in dimorphic forms, α (m.p. 106·6° C.) and β (m.p. 116·8° C.), has been recently investigated by Singh and (Miss) Seth (*unpublished results*); its transformation temperature has also been determined by the application of this method.

*dl*-Camphor-β-sulphonyl-*o*-tolylamide, now prepared by us melts at 98·5° C., whereas in the earlier communication[1] its melting point was given as 103·6° C. The mixed melting point-composition diagram (Fig. 3 B) of *d*-camphor-β-sulphonyl-*o*-tolylamide, m.p. 110° C. with the *dl*-isomeride, m.p. 103·6°, is reproduced from the previous communication.[1] Though each diagram (Figs. 3 A and 3 B) is made up of three curves indicating the racemic forms to be true *dl*-compounds, they are however different in their shapes.

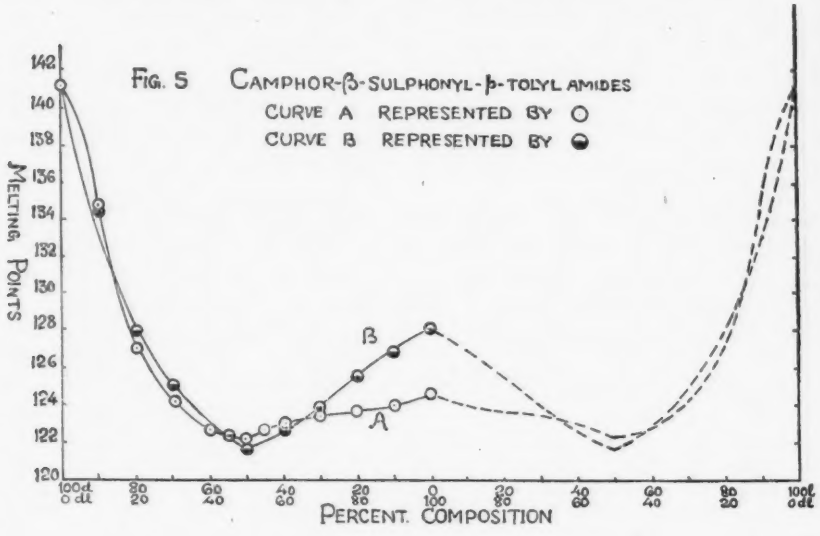
*d*-Camphor-β-sulphonyl-*m*-tolylamide was obtained melting at 100° C., whereas previously its melting point was reported as 93° C. In our earlier experiments we sometimes obtained the lower melting form (93·0° C.) but




subsequently all attempts to isolate this form were unsuccessful. The diagram of the mixtures of the *d*-form, m.p. 100° C., with the *dl*-isomeride is given in Fig. 4 A; that of the *d*-form, m.p. 93° C., with the *dl*-isomeride (Fig. 4 B) is reproduced from the previous communication.[1] Both the diagrams consist of three curves indicating them to be true *dl*-compounds.



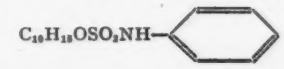
*dl*-Camphor-β-sulphonyl-*p*-tolylamide was obtained melting at 124·5° C., whereas its m.p. in the earlier communication[1] was reported as 128° C. The diagram of the mixtures of *d*-camphor-β-sulphonyl-*p*-tolylamide, m.p. 141·2° C. and the *dl*-isomeride m.p. 124·5° C. is given in Fig. 5 A. The diagram (Fig. 5 B) for the mixtures of the *dl*-form, m.p. 128° C. and the *d*-isomeride is reproduced from the previous paper.[1] The two diagrams are very similar in the first portion upto the eutectic point. But they somewhat differ in the portion lying between the eutectic point and the melting point of the *dl*-isomerides. As in the other cases, the diagrams (Figs. 5 A and 5 B) consist of three curves indicating them to be true *dl*-compounds.




As we have not been able to isolate these abovementioned second forms with a different melting point except sometimes in the case of *d*-camphor-β-sulphonyl-*m*-tolylamide as reported above, we are not in a position to state at this stage that they are dimorphic forms.

## EXPERIMENTAL

### *d-Camphor-β-sulphonylphenylamide, (α- and β-forms)*




*d*-Camphor-β-sulphonylphenylamide occurs in two dimorphous forms. It was prepared by condensing *d*-camphor-β-sulphonyl-chloride with aniline

## TABLE V

*The Rotatory Dispersion of* d-*Camphor-β-sulphonyl-α-naphthylamide, m.p.* 139° *C. in Different Solvents at* 35° *C.* (*S. R. K. Murty*)

| Solvents | Methyl alcohol | | Ethyl alcohol | | Pyridine | | Benzene | |
|---|---|---|---|---|---|---|---|---|
| Conc. in gm. per 100 c.c. | 1·000 | | 1·000 | | 1·000 | | 1·000 | |
| Calc. $[\alpha]_{\lambda}^{35°}$ | $\frac{8\cdot221}{\lambda^2-0\cdot1069}$ | | $\frac{10\cdot39}{\lambda^2-0\cdot0829}$ | | $\frac{11\cdot4}{\lambda^2-0\cdot0769}$ | | $\frac{20\cdot45}{\lambda^2-0\cdot0533}$ | |
| Calc. $\lambda_0$ Å | 3210 | | 2880 | | 2773 | | *2308* | |
| Lines | *o* | *c* | *o* | *c* | *o* | *c* | *o* | *c* |
| 6708 | +24·0° | +23·99° | +28·5° | +28·30° | +31·0° | +30·56° | +51·5° | +51·56° |
| 6438 | 26·5 | 26·73 | 31·5 | 31·32 | 33·0 | 33·76 | 57·5 | 56·62 |
| 6104 | 31·0 | 30·96 | 35·0 | 35·87 | 39·0 | 38·56 | 63·5 | 64·06 |
| 5893 | 34·0 | 34·22 | 39·0 | 39·30 | 42·5 | 42·16 | 70·0 | 69·58 |
| 5780 | 36·0 | 36·19 | 42·0 | 41·35 | 44·5 | 44·32 | 73·0 | 72·83 |
| 5468 | 43·0 | 42·81 | 47·0 | 48·06 | 51·0 | 51·31 | 83·0 | 83·24 |
| 5461 | 43·0 | 42·98 | 47·0 | 48·25 | 51·5 | 51·50 | 83·0 | 83·51 |
| 5209 | 50·0 | 50·0 | 55·5 | 55·13 | 59·5 | 58·62 | 95·0 | 93·8 |
| 5086 | 53·0 | 54·18 | 57·5 | 59·09 | 63·5 | 62·69 | 97·0 | 99·56 |
| 4800 | 66·0 | 65·63 | 71·5 | 70·42 | 74·5 | 74·25 | 118·0 | 115·4 |
| 4678 | 70·5 | 73·41 | 77·0 | 76·38 | 80·0 | 80·26 | 123·5 | 123·5 |
| 4603 | .. | .. | 79·0 | 80·58 | 84·0 | 84·48 | 129·0 | 129·0 |
| 4358 | .. | .. | 95·5 | 96·99 | 100·0 | 100·8 | 150·0 | 149·6 |

## TABLE VI

*The Rotatory Dispersion of* d*-Camphor-β-sulphonyl-β-naphthylamide, m.p.* 131·8° *C. in Different Solvents at* 35° *C. (S. R. K. Murty)*

| Solvents | Methyl alcohol | | Ethyl alcohol | | Acetone | | Chloroform | | Benzene | |
|---|---|---|---|---|---|---|---|---|---|---|
| Conc. in gm. per 100 c.c. | 1·000 | | 1·000 | | 1·000 | | 1·000 | | 1·000 | |
| Calc. $[\alpha]_\lambda^{35°}$ | $\frac{5·648}{\lambda^2-0·0901}$ | | $\frac{6·446}{\lambda^2-0·0797}$ | | $\frac{8·532}{\lambda^2-0·0678}$ | | $\frac{22·8}{\lambda^2-0·0639}$ | | $\frac{37·31}{\lambda^2-0·066}$ | |
| Calc. $\lambda_0$ Å | 3002 | | 2823 | | 2604 | | 2528 | | 2581 | |
| Lines | *o* | *c* | *o* | *c* | *o* | *c* | *o* | *c* | *o* | *c* |
| 6708 | 15·5° | 15·70° | 16·75° | 17·42° | 22·0° | 22·32° | 59·0° | 59·06° | 97·5° | 97·34° |
| 6438 | 17·5 | 17·42 | 19·25 | 19·26 | 25·0 | 24·60 | 65·0 | 65·03 | 108·5 | 107·3 |
| 6104 | 20·0 | 20·0 | 22·25 | 22·02 | 28·0 | 28·0 | 73·0 | 73·86 | 122·0 | 122·0 |
| 5893 | 22·0 | 21·97 | 24·25 | 24·10 | 30·0 | 30·54 | 81·0 | 80·46 | 132·0 | 132·9 |
| 5780 | 23·5 | 23·15 | 25·5 | 25·34 | 32·5 | 32·03 | 85·0 | 84·37 | 142·5 | 139·5 |
| 5468 | 27·0 | 27·04 | 29·75 | 29·40 | 37·0 | 36·90 | 97·5 | 96·96 | 161·5 | 160·5 |
| 5461 | 27·0 | 27·14 | 29·75 | 29·49 | 37·0 | 37·03 | 97·5 | 97·29 | 161·5 | 161·1 |
| 5209 | 31·0 | 31·17 | 33·25 | 33·65 | 42·0 | 41·92 | 109·0 | 109·9 | 183·0 | 182·3 |
| 5086 | 33·5 | 33·50 | 35·25 | 36·00 | 45·5 | 44·69 | 117·0 | 117·0 | 193·0 | 194·2 |
| 4800 | 40·5 | 40·26 | 41·65 | 42·78 | 52·75 | 52·47 | 137·0 | 137·0 | 227·5 | 227·8 |
| 4678 | 43·5 | 43·84 | 46·25 | 46·31 | 57·0 | 56·45 | 145·0 | 147·1 | 251·0 | 245·0 |
| 4603 | 46·5 | 46·41 | 49·75 | 48·79 | 61·5 | 59·24 | 151·5 | 154·1 | 257·0 | 256·9 |
| 4358 | 56·0 | 56·53 | 62·0 | 58·45 | 74·0 | 69·81 | 187·0 | 180·8 | 301·75 | 302·4 |

in equimolecular proportions in the presence of pyridine. The reaction mixture was refluxed on water-bath (using air condenser) for twelve hours. It was poured into excess of cold water and the product solidified on scratching. The crude product was recrystallised from 50 per cent. aqueous alcohol (with animal charcoal) in fine colourless needles m.p. 120° C. (β-form) as found by Singh *et al.* who obtained it in only one form.

*α-form, m.p.* 115° *C.*—The α-form was obtained by recrystallising the abovementioned product (β-form) from aqueous alcohol (90% or more) as rectangular plates, m.p. 115° C.

S (Found) = 10·47; $C_{16}H_{21}O_3NS$ requires S = 10·40%

*β-form m.p.* 120° C.—The β-form was obtained, as above mentioned, by recrystallising the product from aqueous alcohol (less than 75%) as fine needles melting at 120° C.

*Mutual Transformation of α- and β-forms*

(*a*) *From α-form to β-form.*—(i) The α-form was transformed into the β-form by heating it with a trace of the latter.

(ii) The α-form was also converted into the β-form by recrystallising it from aqueous alcohol (50%) when needle-shaped crystals, m.p. 120° C., were obtained.

(iii) On heating the α-form alone at its melting point, the solid which was recovered, remelted at 120° C.

(*b*) *From β-form to α-form.*—The β-form could not be transformed into α-form in the solid state but when dissolved in concentrated alcohol (90 per cent. or more) and allowed to crystallise, it was obtained as rectangular plates melting at 115° C.

The changes are represented below diagrammetically:—

(i) by heating the solid α-form with a trace of β-form;

(ii) by crystallising α-form out of 50% aqueous alcohol;

(iii) by heating α-form alone at its melting-point;

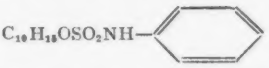
α-form (i), (ii) and (iii) → β-form

(m.p. 115° C.) ← (iv) (m.p. 120° C.)

(iv) By crystallising out of strong aqueous alcohol (90% or more).

The rotatory dispersions* of both the forms were found to be identical in all the solvents and are given in Tables I *a* and I *b*. They are also plotted as $1/[\alpha]_\lambda$ against $\lambda^2$ as straight lines (Fig. 1). The graphs of both the forms in all the seven solvents superpose on each other. These results giving identical values of specific rotations and dispersions prove α- and β-forms to be dimorphous.

*dl-Camphor-β-sulphonylphenylamide*



The compound was prepared as already described by one of us (*Ibid.*)[1] as fine colourless needles melting at 99·0° C. It could not be obtained in dimorphic forms.

TABLE VII

*Camphor-β-sulphonyl phenylamides, Fig.* 2

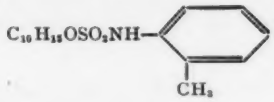
*Mixed melting points of the racemic modification with the* d-*form*

| % of *d*-isomeride α-form or β-form | % of *dl*-isomeride | Mixed m.p. of *d* α-form with *dl*-isomeride °C. | Mixed m.p. of *d* β-form with *dl*-isomeride °C. |
|---|---|---|---|
| 100 | 0 | 115·0 | 120·6 |
| 99 | 1 | 120·0 | 120·0 |
| 97·5 | 2·5 | 119·4 | 119·4 |
| 95 | 5 | 118·8 | 118·8 |
| 94 | 6 | 118·7 | 118·5 |
| 93 | 7 | 118·6 | 118·0 |
| 90 | 10 | 118·2 | 116·6 |
| 80 | 20 | 115·3 | 112·6 |
| 70 | 30 | 108·1 | 105·2 |
| 60 | 40 | 101·7 | 100·5 |
| 50 | 50 | 99·0 | 98·2 |
| 40 | 60 | 97·6 | 96·9 |
| 30 | 70 | 97·8 | 97·4 |
| 20 | 80 | 98·1 | 97·8 |
| 10 | 90 | 98·6 | 98·4 |
| 5 | 95 | 98·7 | 98·6 |
| 0 | 100 | 99·0 | 99·0 |

The mixed melting points of both the dimorphic forms (α and β) of *d*-camphor-β-sulphonyl phenylamide in different proportions were found to be 120·6° (m.p. of the β-form).

* The rotatory dispersion of β-form (m.p. 120° C.) reported previously[12] is identical with that now found.

*d-Camphor-β-Sulphonyl-o-tolylamide*



The compound was prepared in the same way as previously described by Singh *et al.*[1] as fine colourless needles melting at 110° C.

The rotatory dispersion in seven solvents is given in Table II.

The *dl*-isomeride of this compound was prepared in the same way as the *d*-isomeride as colourless hexagonal plates, m.p. 98° C. The previous workers,[1] however, obtained it in colourless needles, m.p. 103·6° C.

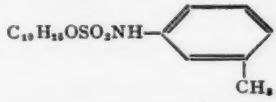
S (Found) = 10·10; $C_{17}H_{23}O_3NH$ requires S = 10·00%.

TABLE VIII

*Camphor-β-Sulphonyl-o-tolylamides, Fig. 3 A*
*Mixed melting points of the racemic modification with the d-form*

| % of *d*-isomeride | % of *dl*-isomeride | Mixed melting point ° C. |
|---|---|---|
| 100 | 0 | 110·0 |
| 90 | 10 | 107·8 |
| 80 | 20 | 105·6 |
| 70 | 30 | 103·6 |
| 60 | 40 | 99·6 |
| 50 | 50 | 96·4 |
| 45 | 55 | 94·4 |
| 40 | 60 | 95·2 |
| 30 | 70 | 96·6 |
| 20 | 80 | 97·3 |
| 10 | 90 | 97·7 |
| 0 | 100 | 98·0 |

*d-Camphor-β-sulphonyl-m-tolylamide*



This compound was prepared by the same method as that given by Singh, Panicker and Ranganathan[1] as prismatic needles. It melted at 100° C. instead of 93° C. as reported by them.

S (Found) = 9·84; $C_{17}H_{23}NO_3S$ requires S = 10·0%.

The rotatory dispersion of the *d*-isomeride in seven solvents is given in Table III.

The *dl*-isomeride of the compound was prepared in the same way as the *d*-isomeride as prismatic needles m.p. 99·5° C.

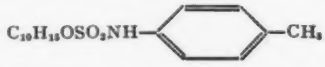
The mixed melting point-composition diagram of *d*-form (m.p. 93° C.) and *dl*-form (m.p. 99° C.) previously described (Fig. 4 B) is reproduced for comparison with that obtained with the *d*-form (m.p. 100° C.) and *dl*-form m.p. 99·5° C. (Fig. 4 A).

TABLE IX

*Camphor-β-Sulphonyl*-m-*tolylamides, Fig.* 4 *A*
*Mixed melting points of the racemic modification with the* d-*form*

| % of *d*-isomeride | % of *dl*-isomeride | Mixed melting-point °C. |
|---|---|---|
| 100 | 0 | 100·0 |
| 90 | 10 | 95·4 |
| 80 | 20 | 93·4 |
| 70 | 30 | 92·4 |
| 60 | 40 | 91·9 |
| 55 | 45 | 91·8 |
| 50 | 50 | 92·2 |
| 45 | 55 | 92·8 |
| 40 | 60 | 93·5 |
| 30 | 70 | 96·2 |
| 20 | 80 | 98·0 |
| 10 | 90 | 99·0 |
| 0 | 100 | 99·5 |

*d-Camphor-β-Sulphonyl-p-tolylamides*




This compound was prepared in the same way as the *ortho* and *meta* isomerides. It crystallised as prismatic needles, m.p. 141·2° C.

Its rotatory dispersion in seven solvents is given in Table IV.

The *dl*-isomeride of this compound was prepared as prismatic crystals, m.p. 124·5° C., whereas the previous workers[1] report its melting point as 128·0° C.

S (Found) = 10·18; $C_{17}H_{23}O_3NS$ requires S = 10·0%.

TABLE X

*Camphor-β-Sulphonyl-*p*-tolylamides, Fig. 5 A*
*Mixed melting points of the racemic modification with the* d*-form*

| % of *d*-isomeride | % of *dl*-isomeride | Mixed melting point of *d*-isomeride with its *dl*-form ° C. |
|---|---|---|
| 100 | 0 | 141·2 |
| 90 | 10 | 134·8 |
| 80 | 20 | 127·0 |
| 70 | 30 | 124·2 |
| 60 | 40 | 122·7 |
| 55 | 45 | 122·4 |
| 50 | 50 | 122·2 |
| 45 | 55 | 122·6 |
| 40 | 60 | 123·0 |
| 30 | 70 | 123·4 |
| 20 | 80 | 123·6 |
| 10 | 90 | 123·9 |
| 0 | 100 | 124·5 |

The mixed melting point-composition diagram of *d*-form (m.p. 141·2° C.) with *dl*-form (m.p. 128° C.) previously described (Fig. 5 B) is reproduced for comparison with that obtained with the *dl*-form (m.p. 124·5° C.) Fig. 5 A.

[With S. R. K. Murty

d-*Camphor-β-sulphonyl-α-naphthylamide and* d-*Camphor-β-sulphonyl--β-naphthylamide*

$C_{10}H_{15}OSO_2NH \cdot C_{10}H_7$ (α- and β-)

These compounds were prepared according to the methods of Singh *et al.*[1] The rotatory dispersions of these compounds in different solvents are recorded in Tables V and VI. It is found that the specific rotatory powers in methyl alcohol and ethyl alcohol of *d*-camphor-β-sulphonyl-α-naphthylamide are greater by about 50% than those of *d*-camphor-β-sulphonyl-β-naphthylamide, whereas in benzene the case is reverse as the specific rotatory powers of the former compound are only about one half of the latter.]

The rotatory dispersion measurements were made in 1% solution in different solvents at 35° C. for 13 wavelengths ($\lambda = 6708$ Å to $\lambda = 4358$ Å)

in the visible region of the spectrum. The values of $\lambda_0$, calculated from the dispersion formulæ, are given in the Tables I *a*–VI.

The melting point-composition diagrams were prepared as follows: an intimate mixture of the racemic compound and the dextro isomeride was prepared by taking exact weights of the components in different proportions in an agate mortar and thorough mixing and grinding. Six determinations of the melting point (capillary tube method) of each mixture were made with Siebert and Kühn thermometers graduated to 0·2° C. and the mean value was taken as the melting point of the mixture. The results are recorded in Tables VII–X. The melting point-composition diagrams are given in Figs. 2, 3, 4 and 5.

## SUMMARY

The rotatory dispersion of *d*-camphor-β-sulphonyl phenylamide, *d*-camphor,-β-sulphonyl tolyl (*o*-, *m*- and *p*-) amides and *d*-camphor-β-sulphonyl naphthylamides (α- and β-) have been determined in 7 solvents for 13 wavelengths ($\lambda = 6708$ Å to $\lambda = 4358$ Å) in the visible region of the spectrum. It is found to be '*simple*' as it can be expressed by the *one-term* Drude's equation, $[\alpha]_\lambda = k/\lambda^2 - \lambda_0^2$. It is controlled generally by a low frequency corresponding to the ketonic group of camphor and sometimes by a high frequency 'characteristic' of saturated molecules. In solvents of *low* dielectric constants such as ethyl acetate, chloroform and benzene, the high frequency corresponding to the saturated molecules sometimes replaces the low frequency pertaining to the ketonic group. The effect of position isomerism and the influence of the solvent on the rotatory power have been also discussed.

*d*-Camphor-β-sulphonyl-phenylamide exists in dimorphic form (α and β). This is established by the identity of their rotatory dispersions and their mutual transformation. A new method for the determination of Transformation (Transition) Temperature of the dimorphic forms, based on Roozeboom's mixed melting point-composition diagram, has been developed. By the application of this method the temperature of Transformation of α- into β-form, in this case, is found to be 118·8° C.

## ACKNOWLEDGEMENT

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# TRANSITION PHENOMENA AT SATURATION TEMPERATURE

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## Introduction

Abrupt transitions in homogeneous systems are normally unexpected during gradual changes in either the composition or in the physical factors such as temperature or pressure. As typical exceptions we have $\lambda$-point of liquid helium as well as the micelle formation in soap solutions. Recent work has shown that ultrasonic absorption by xenon[1] and sulphur fluoride[2] shows a maximum, as the system passes through the neighbourhood of the critical point although there is no heterogeneity developed in the system. This has been accounted for as caused by clustering when the substance is at low concentrations and due to development of holes when the substance is at high concentrations. Similarly the ultrasonic absorption,[3] the molar heat capacity at constant pressure[4] and the viscosity[5] of a binary liquid mixture are found to be maximum in the neighbourhood of the critical solution temperature, although there is no development of heterogeneity. Similarly carbon dioxide[6] shows large molar heat capacity at constant volume near the critical point although there is no heterogeneity developed. The interesting results of Dodd and Hu Pak Mi[7] have shown that the viscosity of phenyl ether shows a transition when the liquid passes through the melting point, when cooled (avoiding solidification ) from the ordinary liquid to the supercooled state. Work in this laboratory (Doss, Gupta and Vishnu)[8] has shown that similar transition occurs in electrical conductivity when molasses (mother liquor left after commercial crystallisation of sugar from sugarcane juice by concentrating and cooling) passes through the saturation temperature, as it is cooled (avoiding crystallisation) from the unsaturated state to the super-saturated state. It was considered desirable to investigate some well defined systems from this point of view. Accordingly the electrolytic conductivity of aqueous solutions of sucrose containing electrolytes, lithium chloride and potassium chloride, has been studied over a temperature range covering the saturation temperature.

## Experimental

Chemicals used were all of C.P. quality. The salt was dissolved in the required quantity of water. The resulting solution was saturated with pure sucrose by keeping the mixture stirred in a thermostat maintained correct to $\pm 0{\cdot}05°$ C. The crystal and the mother liquor were separated by hot centrifuging. The centrifugate was transferred to a tubular conductivity cell (cell

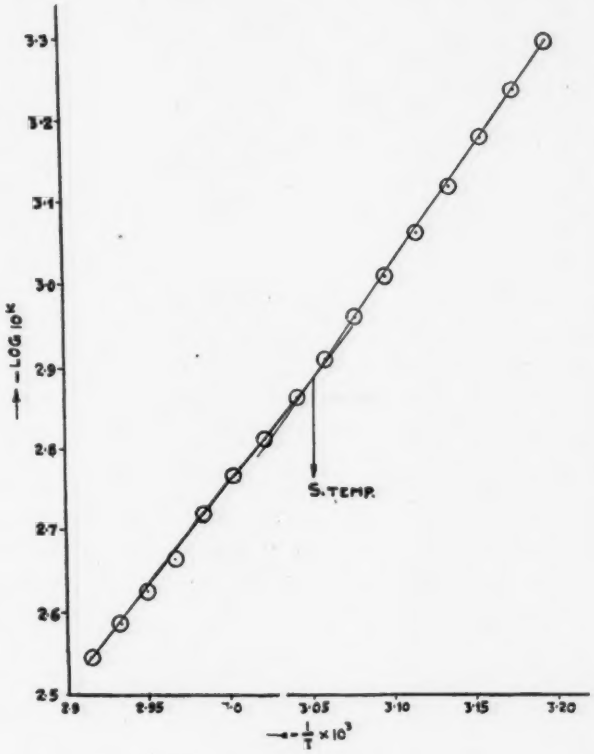


Fig. 1

K = Specific conductance.

T = Absolute temperature.

Composition of the solution:—

10 gm. lithium chloride dissolved in 22·6 gm. water and saturated with sucrose at 55° C.

constant near about 30) containing platinised platinum wire electrodes. The tube was immersed in an electrically maintained liquid paraffin thermostat.

The measurements were first taken at the highest temperature. The temperature of the thermostat was then lowered 2–4° at a time and maintained at each temperature for 20–30 minutes before taking the readings. Since the tubular conductivity cell had a small diameter (5 mm.) the temperature equilibrium was quickly attained. The electrolytic conductivity was determined using 1000 cycles a.c. employing the "magic eye" for detecting the null point.

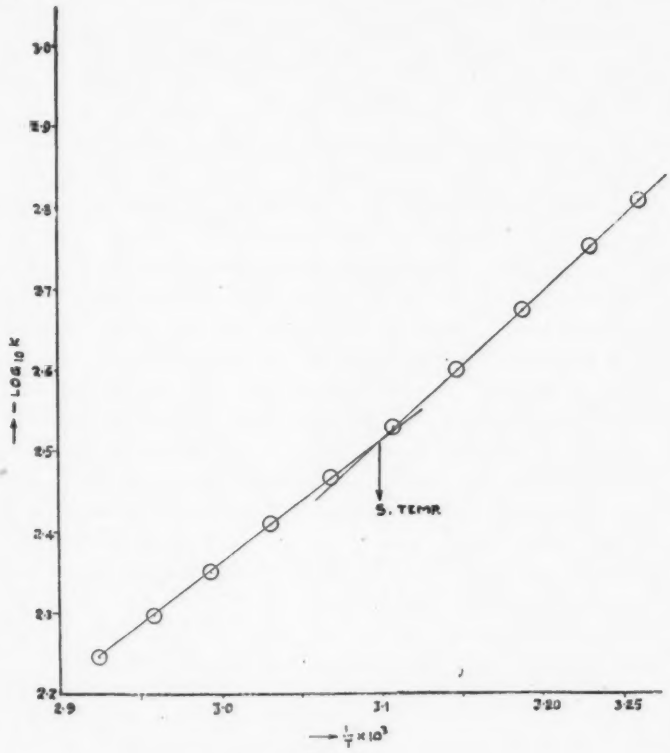


FIG. 2

K = Specific conductance.
T = Absolute temperature.
Composition of the solution:—
10 gm. potassium chloride dissolved in 100 gm. water and saturated with sucrose at 50°.

## RESULTS AND DISCUSSION

The results obtained are shown in Figs. 1 and 2. Logarithm of reciprocal of specific conductance has been plotted against the reciprocal of

absolute temperature. This particular plot was chosen in conformity with Andrade's equation[9] for variation of viscosity with temperature and the well known inverse dependence of conductance on viscosity. It is found

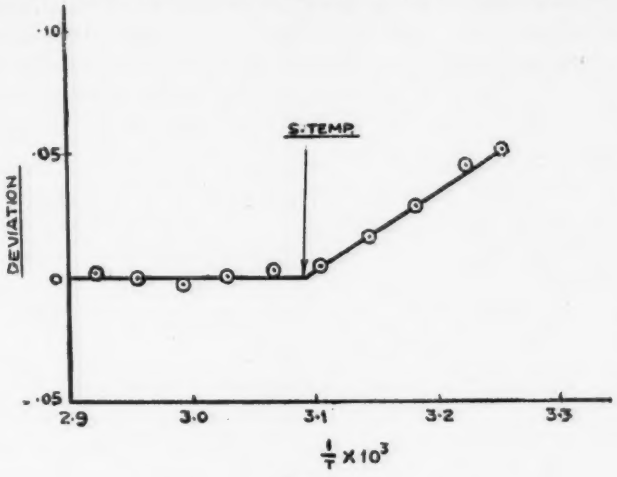


FIG. 3

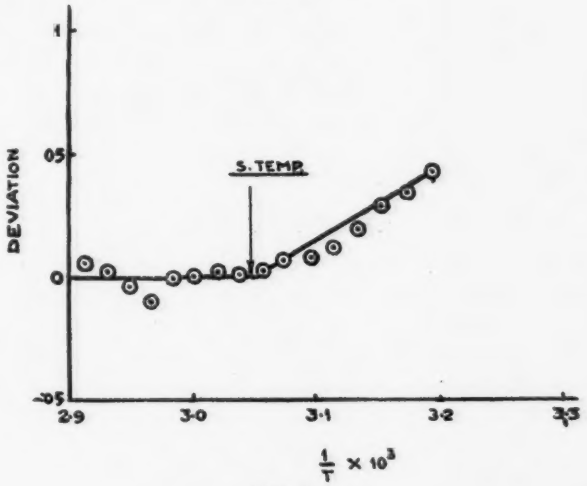


FIG. 4

that the graphs consist of pairs of straight lines intersecting in the neighbourhood of the saturation temperature. This is established beyond question by fitting the best straight line to the points above the saturation temperature

and then plotting deviation from this line as shown in Figs. 3 and 4. The regression equation was first determined statistically for the points above the saturation temperature. The theoretical values of the $-\log_{10} K$ were obtained from the regression equation for the different values of 1/T. The differences between these values and the experimental values are plotted in Figs. 3 and 4. These plots indicate a definite transition at the saturation temperature. It is, however, to be pointed out that the plot for lithium chloride-water-sucrose system, is not good due perhaps to the lower viscosities of the system.

The tubes were throughout perfectly transparent showing that no crystallisation occurred. The transition in electrolytic conductance is to be interpreted as due to the transition occurring in viscosity of the system, presumably due to sudden increase in the development of large clusters of solute molecules below the saturation temperature. Such transitions may be expected to be marked only in highly viscous systems, which may be expected to develop large structures by co-operative orientation.

These results can also be explained on the basis of the "hole" theory of the liquid state.[10, 11] According to this theory the structure of a liquid is characterised by the presence of holes whose size distribution depends on temperature and pressure. The bulk of the substance outside the hole is supposed to have practically the same structure as the corresponding solid. Viscosity is considered to be the outcome of the transfer of momentum by the Brownian movement of the holes and its magnitude is determined by the mean free path of the holes, which in turn depends on their mean lifetime. In a super-saturated system the distribution function of the holes is essentially different from that above the normal saturation temperature, indicating an excess number of very small holes.

## ACKNOWLEDGEMENT

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